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PROCEEDINGS  
OF  
THE SYMPOSIUM  
ON  
PHYSICS OF SOLID STATE

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ALLAHABAD

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# PROCEEDINGS

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VOL. XXV

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PART II

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#### SYMPOSIUM ON THE "PHYSICS OF THE SOLID STATE"

##### INTRODUCTION

By

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The Physics of the Solid State has in recent years engaged considerable attention of physicists and chemists, due to tremendous developments in various fields. In fact, solid physics includes such a wide scope as would naturally render it an unwieldy subject for a symposium. However, the study of any branch of solid physics is profoundly influenced by the results obtained in other branches. The purpose of the present symposium is to bring the problems and results obtained in the different branches together so that the workers in different spheres may mutually benefit each other.

Crystals fascinated early scientists on account of their natural shining surfaces with which they are bounded. With the discovery of X-ray diffraction a way was found for determining the arrangements of the atoms and molecules inside crystals. It was soon discovered that most solid substances when studied by X-ray diffraction showed periodicities in the internal arrangements which are characteristics of crystals. Thus crystallinity is a much more universal property of solids than suspected before. The knowledge of the arrangements of atoms inside a crystal naturally led to attempts to understanding the physical properties of solids on the basis of the mutual interactions of atoms in the lattice.

After some initial successes at determining the structures of crystals, the problem was found to be more and more formidable as more and more complex molecules were confronted. This is because of the fact that there is no way of proceeding straight from the measured reflected intensities to the distribution of electrons inside the crystals that give rise to X-ray reflections. It was shown by Bragg that the periodic distribution of the electron density inside a crystal may be represented by a fourier series of which the amplitude terms are obtainable from the measured intensities. In the fourier series, however, each term includes phase which cannot be obtained from the measured intensities. Although in centrosymmetrical crystals, the phase of any term may take either of the two values 0 and  $\pi$ , even then the ambiguities become too numerous to make any direct synthesis possible. On the other hand if we consider the atoms that are the constituents of the unit cell of a crystal, the problem does not appear to be so formidable in not too complex a substance. We may assume as a first approximation that the constituent atoms are spherically symmetrical and their scattering powers at various angles are known. So the parameters to be determined are only the coordinates of the various atoms. If the number of planes for which intensity measurements are available exceeds the number of unknown parameters one can apply the method of trial and error i.e. to choose the unknown parameters, for which the calculated intensities match the observed ones. The most natural procedure would be to solve the equations that relate the atomic parameters to the structure factors. But apart from the difficulties of solving such equations the structure factors are not known with sufficient accuracy as to warrant a correct evaluation of the atomic parameters by the solution of these equations. If however, the numbers of available intensity measurements are sufficiently large compared to the number of unknown parameters it may be possible to set up a number of equations as well as inequality relations among the structure factors from which in favourable cases it might be possible to fix the phases of the fourier terms unequivocally.

The method of trial and error however, still remains fundamentally the method of structure analysis. This is carried out in two stages. At first a preliminary rough structure is obtained from chemical considerations and matching by trial between the calculated and the observed intensities. In the next stage improvements in Fourier synthesis are successively attempted by manipulating the phases of the Fourier terms. In the first part of the trial, the physical properties e.g. magnetic and optical anisotropies are occasionally of great aid. Patterson showed that the vectors extending from the origin to the peaks in a Fourier summation in which the squares of the structure factors are the amplitude terms, represent the interatomic distances in the crystal. In cases where such peaks are discernible the interatomic vectors are obtained from them and in many favourable cases the atomic parameters may be deduced from these vectors. More recently methods have been evolved for intensifying these peaks and great improvements have also been carried out for deducing the atomic parameters from these vectors. These improvements have enabled crystallographers to probe into the structures of greater and greater complexity.

As regards the second stage, improvements have been attempted from various angles. Since the direct methods as we have seen above do not lead us far, the most important developments have centred round the methods of carrying out as quick fourier summations as possible so as to minimise the enormous time and labour necessary to carry out fourier summations with different phase combinations. Various special types of computers have been developed for the purpose as also the versatile commercial electronic computers have been adapted for the purpose. The method of Pepinsky and the optical methods originally developed by Bragg may be



specially mentioned. On the other hand very useful methods have been found for testing the improvements obtained in the successive trial syntheses. The difference synthesis of Lipson and Cochrane is of great importance as it indicates where improvements are necessary in an actual synthesis. It is highly encouraging to note that the structure of even so complicated a molecule as protein has been tackled with a considerable amount of success.

Knowledge of the internal structures in crystals opened up the possibility of understanding their various physical properties, such as the elastic properties, specific heats etc. The studies of diffuse reflections in Laue photographs have yielded a very convenient way of testing these ideas and thus a very fruitful method for determining the elastic constants of crystals have resulted from these investigations. These measurements again are expected to lead to further understanding of the origin of the various physical properties of crystals. In fact Raman and Vishwanathan have drawn attention to the necessity of a modification of our basic ideas of crystal elasticity. The studies of magnetic properties of crystals have yielded a wealth of informations regarding the fields inside crystals which are responsible for their various physical properties.

There has been a realisation in recent years of the profound importance of imperfections and trace impurities on a number of physical properties particularly luminescence and electrical properties. Discovery of transistor action has revolutionised the electronic techniques. It would be very interesting to see whether extra reflections in Laue photographs of nonthermal origin can throw any light on the imperfections that are of so great importance.

Another fascinating line of research that has developed during recent years is the study of crystal growth. Very interesting results have been obtained regarding spiral growth of crystals by the phase contrast microscopic methods. These studies will help us in understanding the nature of crystalline forces.

The above is only a cross-section of the huge development in the physics of the solid state that has been taking place. The papers that follow will present some of the very interesting aspects of the problems.

# THE POLARIZATION FIELD IN AN IONIC CRYSTAL AND ITS INFLUENCE ON THE RESTSTRAHLEN FREQUENCY

By

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## ABSTRACT

By displacing the lattice of positive ions in an ionic crystal like the alkali halide with reference to the lattice of negative ions, one naturally produces a polarization in the medium. When the displacement is small the polarization may be regarded as due to point-dipoles located at the lattice points of the crystal. Associated with the polarization there will naturally be a polarization field acting on the ions tending to increase this displacement. Knowing the potential energy corresponding to a small displacement, one obviously obtains the reststrahlen frequency of the crystal. In calculating this potential energy, however, one has to include in addition to the work done against the forces due to the Coulomb and the repulsion interactions between the ions, also the work done by the polarization field in effecting this displacement. If the latter work were not included, the frequency that one would get would be that of the individual dipoles isolated from one another, whereas the reststrahlen frequency is that of the assemblage of such dipoles. Owing to their mutual interactions in the assemblage the latter frequency may be markedly different from that of the isolated dipoles. It is precisely these interactions that are taken into account when the effect of the polarization field is included in the calculation of the potential energy.

The characteristic frequencies that appear in the well known Drude formula for dispersion are the resonance frequencies of the medium, in which the effect of the polarization field has been included automatically, and hence the formula will be of general validity irrespective of the magnitude of the polarization field acting on the oscillators. On the other hand in the Lorentz formula, in which the polarization field is taken into account explicitly, the characteristic frequencies that occur are those which the oscillators constituting the medium would have if they had been isolated from one another, i.e., if there had been no polarization field to influence them.

The paper includes also a discussion on the nature of the polarization field in ionic crystals.

## 1. INTRODUCTION

Some years ago we calculated the frequency and the anharmonicity of the polar oscillations of the alkali halide crystals (Krishnan and Roy 1950 ab, 1951) on the basis of the following simple model. The positive and the negative ions in the crystal lattice are regarded as held in their respective positions of equilibrium by the electrostatic and the repulsion interactions between the ions. Whereas the electrostatic interactions are long range ones, the repulsion interactions are practically confined to the adjacent ions only. Now displacing the lattice of positive ions in the crystal with respect to that of the negative ions by a small distance  $r$ , the potential energy due to such a relative displacement may be readily calculated on the basis of this model, and expressed as a power series in  $r$ , in which, owing to the centre of symmetry of the lattice points of the crystal, the terms involving the odd powers of  $r$  will be absent. The coefficient of the  $r^2$  term in this expression will obviously determine the frequency, and that of the  $r^4$  term the anharmonicity, of the polar oscillations of the crystal. For most of the alkali halides, the frequency thus obtained was found to agree closely with the known reststrahlen frequency of the crystal. It was further found that the sign and the magnitude of the anharmonicity calculated in this manner for KCl crystal fitted well with the known decrease of the specific heat

of the crystal at constant volume with increase of temperature at high temperatures. Among the alkali halides this happens to be the only crystal for which such specific heat data are available.

Now the relative displacement  $r$  of the positive and the negative lattices naturally leads to a homogeneous polarization of the crystal, and in calculating the  $r^2$  term in the expression for the potential energy we had to take into account, in the paper referred to, besides the electrostatic and the repulsion interactions between the ions, separately the work done by the polarization field also in effecting this displacement.

A question has been raised in the course of some discussions on the subject whether in considering the electrostatic interactions with all the surrounding ions in the crystal, all of them occupying their respective displaced positions, the effect of the polarization field also has not been indirectly taken into account. The answer to this question is an unambiguous one, namely, that in calculating the reststrahlen frequency one should take into account explicitly the effect of the polarization field, in addition to taking into account the effect of the electrostatic and the repulsion interactions. Even so, the very posing of the question points to the need for a further elucidation of the issues involved. Such an elucidation incidentally helps also to clarify some of the basic concepts regarding the nature of the polarization field itself.

## 2. CALCULATION OF THE RESTSTRAHLEN FREQUENCY

Since our main purpose is the elucidation of the basic issues, and it can be done with any typical crystal, we shall confine attention for the present to a crystal of the NaCl type. Again, since we are concerned here with the calculation of the frequency only, and not its anharmonicity, we shall retain the  $r^2$  term alone in the expression for the potential energy. Knowing the potential energy  $W$  per pair of ions, the frequency of the polar oscillations of the crystal may be readily obtained from the relation

$$W = \frac{1}{2} \mu \omega_0^2 r^2, \quad (1)$$

where  $\omega_0$  is  $2\pi$  times the frequency, and  $\mu$  is the reduced mass of the ion-pair.

Considering now the calculation of  $W$ , it is found that the contribution to  $W$  from the electrostatic interactions between the ions is nothing, owing to the centre of symmetry of the lattice points, and that from the repulsion interactions is given by  $a_1 r^2$ , where

$$a_1 = 3/(2 N \beta d^3) = \alpha e^2 (\delta - 2)/(6d^3); \quad (2)$$

$d$  is the distance between the neighbouring ions,  $\alpha$  is the Madelung constant,  $N$  is the number of ion-pairs per unit volume of the crystal,  $\beta$  is the compressibility, and  $\delta$  is a number which defines the repulsion interaction between two adjacent ions as a function of the distance of separation  $R$  between them :

$$\phi = A \exp (-\delta R/d). \quad (3)$$

Now the relative displacement of the two lattices will produce a homogeneous polarization in the medium, both directly as a result of this separation, and indirectly by polarizing the ions themselves, i.e., by displacing the electronic cloud in each ion relatively to its nucleus. As a result of this polarization there will be a polariz-

ation field acting on the ions, which will be in a direction that will help the further relative separation of the ions. Hence  $a_1 r^2$  will be correspondingly too high an estimate of the potential energy  $W'$  required for the calculation of the reststrahlen frequency  $\omega_0$  with the help of equation (1).

Let  $B_r$  be the total polarization per unit volume. Then  $p/B_r$  will be the polarization field acting on an ion, where  $p$  is the polarization field factor. The corresponding contribution to the potential energy will then be

$$a_2 r^2 = -\frac{1}{2} \epsilon p B_r r^2, \quad (4)$$

where  $\epsilon$  is the magnitude of the electronic charge. Hence the net value of the potential energy per pair of ions due to the relative displacement  $r$  of the two lattices, will be given by

$$W' = (a_1 + a_2) r^2 = a r^2, \text{ say.} \quad (5)$$

We shall quote here some of the major results obtained in the papers referred to, relating to the quantities involved in (5) and relevant to our purpose.

1. Since the relative displacement  $r$  of the two lattices is small in comparison with the inter-ionic distance  $d$ , the detailed structure of the polarization due to this displacement corresponds to locating at each point of the lattice of positive ions a point dipole of moment  $\epsilon r$ , with its direction along that of  $r$ .

2. The polarization field associated with the ionic displacements  $r$  was found to have just the Lorentz value, namely  $4\pi/3$  times the polarization per unit volume, which is to be expected since the medium consists now of point dipoles occupying the points of a simple cubic lattice, and Lorentz's original calculation which led to the factor  $4\pi/3$  was concerned specifically with this case.

3. It was further found that the relative displacement of the two lattices does not induce any electronic polarization in the ions, and hence the total polarization per unit volume is just  $N\epsilon r$ .

The experimental evidence for this finding is this. The observed reststrahlen frequency is just what should be expected if the total polarization of the medium had been  $N\epsilon r$  per unit volume. Any appreciable electronic polarization induced by the ionic displacements  $r$ , would have lowered correspondingly the reststrahlen frequency below its observed value.

In other words the mutual interactions between the displacement dipoles  $\epsilon r$  correspond to a polarization field factor  $p = 4\pi/3$ , whereas the interactions between these dipoles and the electronic cloud of the ions correspond to  $p = 0$ . This is due to the following circumstance. The polarization due to the displacement of the electronic cloud with respect to its nucleus cannot be replaced by a point dipole, except for its effect at large distances. The extent of overlap of the electronic clouds of neighbouring ions is obviously such as to make  $p = 0$  for interactions involving electronic polarizations.

In view of these findings, one obtains

$$a_2 r^2 = -\frac{1}{2} \pi N \epsilon^2 r^2 \quad (6)$$

The reststrahlen frequencies of all the alkali halide crystals were calculated in this manner using (1) and (5), and including in (5) explicitly the contribution  $a_2 r^2$  from the polarization field to the potential energy. The calculated frequencies were found to agree well with the observed ones.

### 3. THE FREQUENCIES INVOLVED IN THE DISPERSION FORMULAE OF DRUDE AND LORENTZ

Just as one obtains from the potential energy  $W = ar^2$  a certain frequency  $\omega_0$  which can be identified with the resonance frequency of the crystal, one can also calculate another characteristic frequency  $\Omega_0$  from the expression  $W_1 = a_1 r^2$  using a relation analogous to (1). The difference between  $\omega_0$  and  $\Omega_0$  is that in calculating the former the contribution to the potential energy from the polarization field has been included, whereas in calculating  $\Omega_0$  this contribution has not been included. As was shown by us in some later papers (Krishnan and Roy 1952, 1953)  $\Omega_0$  also has a physical significance. It is the frequency which the individual dipoles located at the lattice points would have, had they been isolated from one another, as distinguished from the reststrahlen frequency  $\omega_0$  which is that of the assemblage of these oscillators. That the resonance frequency  $\omega_0$  of the assemblage is different from the frequency  $\Omega_0$  of the isolated dipoles is indeed to be expected, and is due to the mutual interactions of the dipoles in the assemblage. It was further shown in the papers referred to that the effect of their mutual interactions on their frequency is equivalent to the effect of the polarization field in the assemblage on the frequency.

This manner of distinguishing between  $\omega_0$  and  $\Omega_0$  throws new light on the well-known dispersion formulae of Drude and Lorentz. Again, since we are concerned here with illustrating the basic results, it will be convenient to take the simple case when the medium has just one frequency, namely, the reststrahlen frequency  $\omega_0$ , the corresponding frequency of the isolated oscillators calculated from  $W_1 = a_1 r^2$  being  $\Omega_0$ . Now the dielectric constant of such a crystal for any applied frequency  $\omega$  is given by the relation,

$$K_\omega = 1 + 4\pi x, \quad (7)$$

where  $x$  is the polarization that would be induced in unit volume, per unit field in the medium' as usually defined. If  $\gamma$  is the moment induced in an isolated oscillator per unit field incident on it, then obviously

$$\gamma = \frac{e^2}{\mu(\Omega_0^2 - \omega^2)}. \quad (8)$$

There are  $N$  such oscillators in the medium but  $x$  will not be merely  $N$  times  $\gamma$ , but may differ from it considerably, owing to the mutual interactions of these oscillators.

The effect of these interactions on  $x$ , and hence also on  $K_\omega$ , can be taken into account in two alternative, but equivalent, ways.

1. The actual field producing the polarization in each of the oscillators in the medium, still regarded as retaining its natural frequency  $\Omega_0$ , is not the field in the medium, say  $E$ , but will be greater by  $\frac{4}{3}\pi x E$ , so that

$$x = N\gamma (1 + \frac{4}{3}\pi x) = N\gamma (K_\omega + 2)/3. \quad (9)$$

The expression for  $K_\omega$  then takes the well-known Lorentz form

$$\frac{K_\omega - 1}{K_\omega + 2} = \frac{4}{3}\pi N \frac{e^2}{\mu(\Omega_0^2 - \omega^2)}.$$

2. The alternative way in which the mutual interactions between the dipoles can be regarded as influencing the dielectric constant, is through their effect on the frequency of the oscillators, their frequency  $\omega_a$  in the assemblage being different from that in the isolated state, namely  $\Omega_0$ . The field that produces the polarization in the oscillator is now just the field in the medium  $E$ .

$$\text{In this case} \quad N = \frac{Ne^2}{\mu(\omega_a^2 - \omega^2)} \quad (11)$$

$$\text{and hence} \quad K_\omega = 1 + 4\pi N = \frac{e^2}{\mu(\omega_a^2 - \omega^2)} \quad (12)$$

The two expressions (10) and (12) will become identical when

$$\Omega_0^2 - \omega^2 = \frac{K_\omega + 2}{3} (\omega_a^2 - \omega^2). \quad (13)$$

From (12) one can readily obtain

$$\begin{aligned} K_\omega &= 1 + \frac{\omega_a^2 - \omega^2}{\omega^2} \\ K_\omega &= 1 + \frac{\omega_a^2}{\omega^2} \end{aligned} \quad (14)$$

Eliminating  $\omega$  between (13) and (14) one can see that the criterion for securing the identity of (10) and (12), namely (13), reduces to

$$\Omega_0^2 = \frac{K_\omega + 2}{3} \omega_a^2. \quad (15)$$

It can be readily seen that the values of  $\Omega_0^2$  and  $\omega_a^2$  obtained from  $a_1$  and  $a$  respectively would lead to precisely this relation, since

$$a_1 = \frac{1}{3}\mu\Omega_0^2 = a + \frac{1}{3}\pi Ne^2 = \frac{1}{3}\mu\omega_a^2 \left(1 + \frac{K_\omega - 1}{3}\right). \quad (16)$$

Thus one can readily see that by including in the expression for the potential energy  $W$  the contribution from the polarization field, one obtains the reststrahlen frequency  $\omega_a$  of the medium, i.e. of the assemblage of oscillators, whereas without it one gets the frequency  $\Omega_0$  which the same oscillators would have, had they been isolated from one another.

#### 4. THE NATURE OF THE POLARIZATION FIELD

We now return to the question posed in an earlier section. If the polarization of the medium arises from the relative separation of the lattices of positive and negative ions, and if in obtaining the potential energy from which the reststrahlen frequency is to be calculated the contribution to it from all the positive and the negative ions, in their displaced positions, has been taken into account, is not the effect of the polarization field also included in it automatically? The answer is supplied indirectly by the results obtained in the previous section, and it is quite definite, namely, that the polarization field has to be taken into account separately, since the frequency that we are trying to calculate is the resonance frequency  $\omega_a$  of the crystal, and not  $\Omega_0$  of the corresponding isolated oscillators.

2. The alternative way in which the mutual interactions between the dipoles can be regarded as influencing the dielectric constant, is through their effect on the frequency of the oscillators, their frequency  $\omega_0$  in the assemblage being different from that in the isolated state, namely  $\Omega_0$ . The field that produces the polarization in the oscillator is now just the field in the medium  $E$ .

In this case 
$$\kappa = \frac{Ne^2}{\mu_1 \omega_0^2 - m^2} \quad (11)$$

and hence 
$$K_m = 1 - 4\pi N \frac{e^2}{\mu_1 \omega_0^2 - m^2} \quad (12)$$

The two expressions (10) and (12) will become identical when

$$\Omega_0^2 - m^2 = \frac{K_m + 2}{3} (\omega_0^2 - m^2). \quad (13)$$

From (12) one can readily obtain

$$\frac{K_m - 1}{K_m + 1} = \frac{\omega_0^2 - m^2}{m^2} \quad (14)$$

Eliminating  $\omega$  between (13) and (14) one can see that the criterion for securing the identity of (10) and (12), namely (13), reduces to

$$\Omega_0^2 = \frac{K_0 + 2}{3} \omega_0^2. \quad (15)$$

It can be readily seen that the values of  $\Omega_0^2$  and  $\omega_0^2$  obtained from  $a_1$  and  $a$  respectively would lead to precisely this relation, since

$$a_1 = \frac{1}{3} \mu \Omega_0^2 = a + \frac{1}{3} \pi N e^2 = \frac{1}{3} \mu \omega_0^2 \left(1 + \frac{K_0 - 1}{3}\right). \quad (16)$$

Thus one can readily see that by including in the expression for the potential energy  $W$  the contribution from the polarization field, one obtains the reststrahlen frequency  $\omega_0$  of the medium, i.e. of the assemblage of oscillators, whereas without it one gets the frequency  $\Omega_0$  which the same oscillators would have, had they been isolated from one another.

#### 4. THE NATURE OF THE POLARIZATION FIELD

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One can also approach the question from certain direct considerations regarding the mechanism of the polarization field. Consider a medium of induced point-dipoles arranged in a simple cubic lattice. Consider one of these lattice points, say O. Now the field in the medium  $E$  as usually defined, is that at O when it is made the centre of a very thin long cylindrical cavity scooped out of the medium with its axis along the direction of the polarization. Hence  $E$  will consist of the applied field, if any, and the field due to the charges developed on the surface of the medium as a consequence of the polarization of the medium. The surface charges, and hence the field at O due to them, will obviously be determined by *all* the dipoles in the medium, *including that at O also*. On the other hand, the inner field  $E_i$ , again as usually defined, will be the field at O when the dipole at O is removed without disturbing the surrounding dipoles. Obviously the difference between  $E$  and  $E_i$  is this: whereas the former includes a certain averaged self-field at O due to the dipole at O, the latter does not include it. Since this self-field is negative,  $E$  will be smaller than  $E_i$ . The excess of  $E_i$  over  $E$  is by definition the polarization field. For a cubic distribution of point-dipoles, as Lorentz has shown,

$$E_i = E + \frac{4}{3} \pi \times E, \quad (17)$$

where  $\times E$  is the total polarization per unit volume.

Now one can readily appreciate the equivalence of the two alternative ways described earlier in this paper, of taking into account the effect of the mutual interaction of the dipoles. Consider one of the dipoles say the one at O. It may be regarded as having the frequency  $\Omega_0$  and placed in the cavity, created by removing the dipole at O, and thus subject to a field  $E_i$ , or alternatively as being an integral part of the medium with its frequency the same as that of the medium, namely  $\omega_0$ , the field that determines its polarization being now the field in the medium  $E$ . The difference between  $E_i$  and  $E$ , as we have seen, is  $\frac{4}{3} \pi$  times the polarization per unit volume, i. e.  $\frac{4}{3} \pi N e r$ .

One thus obtains the relations

$$\left. \begin{aligned} 2a_1 r &= \mu \Omega_0^2 r = E_i e \\ 2a r &= \mu \omega_0^2 r = E e \end{aligned} \right\} (18)$$

from which one further obtains

$$a - a_1 = a_2 = \frac{1}{2} (E - E_i) e / r = -\frac{2}{3} \pi N e^2, \quad (19)$$

which is just equation (6).

The relations will again be consistent with the expression for the potential energy per unit volume of the crystal due to the relative separation of the lattices of positive and negative ions, namely,

$$NW = N a r^2 = \frac{1}{2} N \mu \omega_0^2 r^2 = (K_0 - 1) E^2 / (8 \pi), \quad (20)$$

from which one obtains

$$K_0 - 1 = \frac{4 \pi N e^2}{\mu \omega_0^2}, \quad (21)$$

which is just relation (12) in the relevant special case when  $\omega = 0$ .



## 5. SOME GENERAL CONSIDERATIONS

Returning to the calculation of the potential energy  $W$ , one may re-examine here the contributions from the electrostatic and the repulsion interactions. The repulsion interactions are confined practically to the nearest neighbours, and there is no ambiguity in calculating them. On the other hand, the electrostatic interactions are long-range ones, and in calculating for example the interactions between any two distant ions we have taken the force between them to be given by  $\pm e^2/R^2$ , as though they were *in vacuo*, and we have ignored the presence of the intervening ions. For very distant ions one may take the intervening medium as having the appropriate dielectric constant  $K$  so that the force between them is now  $\pm e^2/(KR^2)$ . But for the nearer ions the effective value of the dielectric constant to be used in this expression will be difficult to estimate. In any case the usual calculation of the interactions in which the presence of the intervening ions is ignored, which is equivalent to putting  $K=1$ , is obviously not justifiable. It may appear at first sight that by taking the influence of the intervening ions into account in calculating the electrostatic interactions it may not be necessary to take account explicitly the effect of the polarization field.

This conclusion also would not be justified. It is sufficient to mention in this connection that the actual contribution from the electrostatic interactions to the  $r^3$  term in the expression for  $W$  is nothing, and even if the appropriate dielectric constants were to be taken into account in calculating the electrostatic forces their contribution to the  $r^3$  term would still be zero because of the cubic symmetry of the lattice, though the contribution to the  $r^4$  term will be affected.

Thus we are forced to the same conclusion as previously, namely, that in calculating the potential energy  $W$ , and thence the reststrahlen frequency  $\omega_0$ , the contribution to  $W$  from the polarization field has to be explicitly taken into account. Otherwise the frequency that one obtains would be that of the isolated oscillators, namely  $\Omega_0$ , whereas the reststrahlen frequency is the resonance frequency  $\omega_0$  of the assemblage of these oscillators, which owing to the mutual interaction of these oscillators, may be markedly different from the frequency  $\Omega_0$  of the isolated oscillators.

## 6. THE OVERLAP OF THE ELECTRONIC CLOUDS OF ADJACENT IONS

In the foregoing discussions we have taken the charges on the ions to be  $\pm e$ , where  $e$  is the electronic charge. This will be the case rigorously if the neighbouring ions did not influence each other, i.e., if the electronic clouds of adjacent ions did not overlap appreciably. But actually the overlap will be considerable. The major effect of the overlap from the point of view adopted by us comes to this. As a result of the separation of the positive and the negative lattices there is polarization of the crystal. This polarization might induce the electronic polarization of the ions, i.e. produce a shift of the electronic cloud of an ion relatively to the nucleus of the ion. The effect of the overlap is to make the electronic polarization induced by the relative displacement of the two lattices negligible; while the charges on the ions retain the magnitude of the electronic charge. This method of taking the overlap into account is simple, and fits well, as we have seen, with observation.

On the other hand one may, alternatively, assume the polarization fields, associated not only with the ionic displacement, but also with the shift of the electrons with respect to their nuclei, to have the Lorentz value, and the effective

charges to be correspondingly smaller than  $|e|$  in magnitude. There are some major difficulties in accepting this view. Apart from the difficulty of determining theoretically the magnitude of the overlap, and thence the effective charges on the ions, the polarization field associated with the electronic polarization is known from other phenomena to deviate considerably from the Lorentz field. For example, considering the temperature variation of refractivity, which is practically the variation due to the change in density accompanying the change in temperature—it is found that the terms involving the electronic frequencies behave very differently from the term involving the reststrahlen frequency.

From a detailed analysis of the experimental data for the dispersion, and for its temperature variation, in the alkali halides, Ramachandran (1947) found that in the expression for  $dK\omega/dt$  the term involving the reststrahlen frequency  $\omega_0$  is proportional to  $1/(\omega_0^2 - \omega^2)$ , whereas the terms involving the ultraviolet frequencies  $\omega_i$  are proportional to  $1/(\omega_i^2 - \omega^2)$ , which points to a marked difference in the behaviour of the two sets of frequencies. The difference can be attributed to the reststrahlen oscillators being practically point-dipoles, whereas the electronic oscillators are not. The result will be that the polarization field corresponding to the mutual interactions of the reststrahlen oscillators will have just the Lorentz value, as we have seen, whereas the interactions between the reststrahlen oscillators and the electronic oscillators, or between the electronic oscillators themselves, would be much smaller. Actually the experimental finding quoted above, obtained from the temperature variation of the dispersion, points to the interactions involving the electronic oscillators being negligible. This was precisely also the conclusion to which we were led from the magnitude of the contribution to  $W$  from the polarization field, i.e., the magnitude of  $a_2$  required to explain the observed reststrahlen frequency.

Indeed all the observational data receive a natural and quantitative explanation on the basis of the approximation that the effective charges on the ions are just  $\pm e$  and that the whole effect of the overlap of the electronic clouds of the neighbouring ions is to suppress completely the interactions between the reststrahlen oscillators and the electronic ones, and also those among the electronic oscillators themselves. On the other hand, the mutual interactions between the reststrahlen oscillators among themselves are considerable, and correspond to a polarization field having just the Lorentz value.

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# ON THE STUDY OF ELASTICITY AND SOME OTHER PROPERTIES OF CRYSTALS BY DIFFUSE X-RAY REFLECTIONS

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During the last decade researches involving the use of diffusely reflected X-rays have been carried out in various laboratories in different countries. The work of these laboratories has been to a large extent complementary. In Cambridge, England, we have concentrated mainly on the study of elastic properties but have done some work connected with defects in the regularity of the atomic arrangement and it is mainly with these researches that this article is concerned. The results were worked out in terms of the currently accepted theory of crystal elasticity and in this article no departure from this presentation will be made. However, recent work by Laval,<sup>1,2</sup> Le Corre<sup>3,4,5,6</sup> Viswanathan,<sup>7,8</sup> and Raman and Viswanathan<sup>9,10</sup> throws doubt on the validity of the old theory and a revision of part or the whole of the interpretation of the experimental data may be necessary.

## Experimental technique

Methods of measuring the intensity of X-ray beams have been worked out over the past forty years. The study of Diffuse reflections has much in common with the measurement of normal Bragg reflections. The special features of diffuse reflections are (a) weak intensity and (b) relatively wide angular distribution. The intensities to be measured are usually several thousand times weaker than a Bragg or Laue reflection and this makes the time required for making the observations rather long. The diffuse reflections are usually spread over several degrees and it is the distribution with angle in the neighbourhood of a Laue reflection which is the most important part of the data.

During the last eight years both spectrometer methods and photographic methods have been evolved for this type of study. The application of the Geiger counter spectrometer was described by Wooster, Ramachandran and Lang<sup>11</sup> and by Ramachandran and Wooster.<sup>12</sup> A monitor giving a control over the incident intensity of the X-ray beam was described by Hargreaves, Prince and Wooster.<sup>13</sup> The photographic method of study has been described by Horne and Wooster<sup>14,15</sup> and the automatic recording microdensitometer, which is so valuable in obtaining the distribution of blackening over the diffuse spot has been described by Wooster.<sup>16,17</sup>

Certain general observations may be made concerning the experimental technique and the necessary requirements of the apparatus. If a counter-spectrometer is used the intensity of the incident beam of X-rays must be kept constant or else a continuous record of the ratio of the intensity of the incident beam to that of the diffusely reflected beam must be obtained. On the whole the spectrometer method gives more accurate and direct information concerning the elastic constants than any other. If a counter-spectrometer is not available the usual single-crystal X-ray cameras may be used. It is not usually possible to obtain a sufficiently strong beam of crystal-reflected X-rays for use with a photographic instrument. Filtered radiation is therefore used and the white radiation streak makes it impossible to study a certain portion of the diffuse spot. However, this still allows observations to be made which yield the ratios of the elastic constants

in cubic crystals. The photographic method can only be used with a microdensitometer and for convenience and accuracy this should be automatically recording.

### Interpretation of measurements

The developments which have occurred in the interpretation of the experimental material are more novel than those concerned with the experimental technique. The problem of relating the intensity of the diffusely scattered rays to the elastic constants has been solved in the following way. The thermal vibration of atoms may be regarded as due to the superposition of a large number of wave trains of different wave-lengths and travelling in different directions through the crystal. Each wave train can scatter X-rays in a particular direction and with an intensity depending on the amplitude of the elastic wave. An optical analogy can be used to illustrate this fact<sup>18,19</sup>. Thus a particular direction of diffusely scattered X-rays corresponds to a particular wave-length and wave normal of the elastic waves in the crystal. The precise expression of these principles was first given by Waller<sup>20</sup> and later applied to cubic crystals by Jahn.<sup>21</sup> To facilitate explanation we shall use the Indian word "rekha" to denote a line which joins any point in reciprocal space to the nearest reciprocal lattice point. The word "relp" will be used as an abbreviation for "reciprocal lattice point" and, lastly, "Rel-vector" will denote the line joining a relp to the origin of the reciprocal lattice. Using the Waller-Jahn theory the variation of X-ray scattering with direction can be expressed by a factor  $K$  where  $K$  is given by the expression,

$$K[ABC]_{hkl} = P_l P_k (A_{lk}^{-1})$$

In this expression the symbols have the following meanings;  $A, B, C$ , are integral numbers proportional to the direction cosines,  $u_l$ , of the rekha corresponding to the  $K$ -value,  $h, k, l$  are the indices of the relp,  $P_l$  are the direction cosines of the rel-vector,  $(A_{lk}^{-1})$  is the inverse matrix of  $A_{lk}$  where,

$$A_{lk} = c_{llmk} u_l u_m$$

$c_{llmk}$  are the elastic constants.

We imagine a sphere of unit radius and at each point on the surface of this sphere we write down the  $K$ -value corresponding to the direction passing through that point and the centre of the sphere. All points on the sphere having the same  $K$ -value are joined together thus forming a series of contours. A stereographic projection of the sphere with its contours may be made and this forms a convenient representation of the variation round any relp of the intensity of diffuse X-ray scattering.<sup>22</sup> Fig. 1 shows a diffuse photograph obtained with a lead single crystal (400 relp) and fig. 2 is the  $K$ -surface appropriate for the interpretation of this photograph.<sup>23</sup> It is possible to construct a series of such  $K$ -surfaces for a given relp with different ratios of the elastic constants. Such a set can constitute a standard set for all cubic crystals. It is not necessary to deal with relps other than 100, 110 and 111. If the  $K$ -values for certain definite points on the  $K$ -surface are found experimentally, the problem of deducing the ratio of the elastic constants resolves itself into finding which of a standard set of  $K$ -surfaces best fits the experimental data. This matching may be carried out for two or more relps and gives values of  $c_{12}/c_{11}$  and  $c_{44}/c_{11}$ . If one absolute measurement of  $K$  is made, by comparing the intensity of the direct beam with that of a diffusely reflected beam, the separate value of the constants can be found. This is often difficult to do

with sufficient accuracy and in that case use is made of the cubic compressibility determined by other experimental methods. If the cubic compressibility is  $\beta$ , then

$$\beta = 3/(c_{11} + 2c_{12})$$

and when this value of  $(c_{11} + 2c_{12})$  is combined with the value of  $c_{12}/c_{11}$  the individual values of  $c_{11}$  and  $c_{12}$  may be found. The same method involving the use of K-surfaces can be applied to tetragonal, hexagonal, trigonal and orthorhombic as well as cubic crystals. Monoclinic and triclinic crystals have not so far been studied by this method.

Spectrometer observations are usually made so as to give the diffusely scattered intensity at selected points along chosen rektas. The diffuse intensity is partly due to the thermally excited elastic waves and partly due to Compton scattering and cosmic rays. The former part varies inversely as  $R^2$  where  $R$  is the distance of the point corresponding to the observation from the relp. Thus a plot of the diffuse intensity  $I$  against  $1/R^2$  gives the value of the corresponding  $K$   $[ABC]_{hkl}$ . The elastic ratios are then obtained as described above in connection with the photographs.

### Special features of measurements of elastic constants by diffusely reflected X-rays

Considerable experience has now been obtained in the application of diffuse X-ray reflections to the measurement of elastic constants. In many observations the same, or nearly the same results have been obtained as are given by other methods. This applies to studies on zincblende<sup>24</sup>, KBr, KCl, NaClO<sub>3</sub>, Galena PbS<sup>25</sup>, LiF<sup>26</sup>, diamond<sup>26</sup>, Si<sup>27</sup>, and Ge<sup>28</sup>. Observations on single crystals of lead<sup>29</sup> have given significantly different results from those of other workers. It is clear that no strain is put on the crystal by the reflection of X-rays and when the material is very soft it is not surprising that the older methods have given wrong results. The X-ray measurements determine particular constants more directly than most other methods. Thus lead shows a remarkable anisotropy which is determined principally by  $(c_{11} - c_{12})$ . This quantity is measured directly by one set of X-ray observations, and the result is 50% higher than that obtained by previous investigators.<sup>29,30</sup> A comparison of the elastic constants and moduli is given in table I.

TABLE I

*Values of the elastic constants and moduli of lead determined by dynamic, static and X-ray methods respectively.*

	Goens and Weerts (1936)	Swift and Tyndall (1942)	Prasad and Wooster (in Press)
	dyne. cm. <sup>-2</sup>	dyne. cm. <sup>-2</sup>	dyne. cm. <sup>-2</sup>
$c_{11}$	$4.77 \times 10^{11}$	$4.66 \times 10^{11}$	$5.0(3) \times 10^{11}$
$c_{12}$	4.03	3.92	3.9(3)
$c_{44}$	1.44	1.44	1.4(0)
$c_{11} - c_{12}$	0.74	0.74	1.10
	cm. <sup>2</sup> dyne. <sup>-1</sup>	cm. <sup>2</sup> dyne. <sup>-1</sup>	cm. <sup>2</sup> dyne. <sup>-1</sup>
$s_{11}$	$92.7 \times 10^{-13}$	$92.7 \times 10^{-13}$	$63.2(2) \times 10^{-13}$
$s_{12}$	-42.5	-42.4	-27.7(7)
$s_{44}$	69.4	69.4	71.4(4)
$s_{11} - s_{12}$	135.2	135.2	90.9(9)

Even greater differences are found between the old<sup>31</sup> and X-ray values<sup>32</sup> for white tin. The difference affects mainly the constants concerned with torsion, namely,  $c_{44}$  and  $c_{66}$ . This carries as a consequence a considerable difference between certain of the elastic moduli,  $s_{1k}$ , obtained by the old and new methods. The results are compared in the following table.

TABLE II

*Values of the elastic constants and moduli of white tin determined by classical and by X-ray methods respectively.*

	Bridgman (1925)	Prasad and Wooster (1955)
	dyne. cm. <sup>-2</sup>	dyne. cm. <sup>-2</sup>
$c_{11}$	$8.40 \times 10^{11}$	$8.6 \times 10^{11}$
$c_{33}$	9.67	13.3
$c_{44}$	1.75	4.9
$c_{66}$	0.74	5.3
$c_{12}$	4.87	3.5
$c_{13}$	2.81	3.0
	cm. <sup>2</sup> dyne. <sup>-1</sup>	cm. <sup>2</sup> dyne. <sup>-1</sup>
$s_{11}$	$18.5 \times 10^{-13}$	$14.6 \times 10^{-13}$
$s_{33}$	11.8	8.5
$s_{44}$	57.0	20.6
$s_{66}$	135	19.0
$s_{12}$	-9.9	-5.3
$s_{13}$	-2.5	-2.07

It seems likely that no method involving the application of static strains can apply sufficiently small stresses to leave the crystal as a true single crystal and that some of these discrepancies are due to this cause.

Another important feature of the X-ray method is the small size of crystal to which it can be applied. In principle the size is limited only by the exposure time necessary for the photograph. Generally speaking a diffuse reflection photograph requires several thousand times as long an exposure as a Laue photograph for the same density of the darkening of the film. Thus, for a crystal of low absorption coefficient for X-rays, a size of  $0.5 \times 0.5 \times 0.5$  mm is usually large enough. If the absorption coefficient is heavy so that all reflection is from the surface, then a piece  $1 \times 1 \times 0.1$  mm would generally be suitable. The interpretation of the results is easiest when a flat plate cut parallel to the required atomic plane is used. Such a plate must be thick enough to absorb the whole of the monochromatic radiation incident upon it. The original measurements by Voigt<sup>33</sup> on the elastic constants of iron pyrites,  $\text{FeS}_2$ , were probably made difficult by the small size of crystal available. The same factor may have influenced the work of Doraiswami<sup>34</sup> on the same crystal. Voigt and Doraiswami both found the remarkable result that the elastic modulus  $s_{13}$  was positive. The meaning of this is that if a stretching force is applied parallel to one edge of a (100) cube, then an expansion will occur in a perpendicular direction. This is naturally not to be expected. The subject has been studied by diffuse X-rays by Prasad and Wooster,<sup>35</sup> who find that the positive  $s_{12}$  is not confirmed.

Finally, organic materials, which are soft and can only be fashioned into centimetre-size plates or bars with difficulty, can be examined in the form of small crystals by the X-ray method. The X-ray absorption coefficient is in this case generally small and the crystal can often be used without preparing any face on it at all. An example of an investigation on an organic crystal is the work on hexamethylene tetramine,  $\text{N}_4(\text{CH}_2)_6$ .<sup>12</sup>

### Reciprocal spikes and plates

The results of measurements on diffuse scattering can be used not only for elasticity measurements but also for the study of the various extensions of relps which occur in the form of spikes, plates or other geometrical forms. The spikes associated with the relps of diamond have been studied in a number of laboratories over many years. The contribution of Hoerni and Wooster<sup>26,37</sup> has been to make the rules governing this phenomenon more explicit and to afford some quantitative data. The spikes were shown to be parallel to the axes [100] and to vary in intensity roughly proportional to the inverse square of the distance along the spike from the associated relp. The intensities of the spikes parallel to [100] associated with the relps 1kl, 2kl, 3kl, 4kl were 100, 70, <5, and 30 respectively, independent of the values of k and l. Similar results were obtained for the spikes parallel to the axes [010] and [001]. There are two ways in which attempts may be made to explain the intensities of the spikes; one involves the assumption that particular (100) planes of atoms scatter X-rays anomalously though their centres are in the usual positions, the other approach assumes that the atoms in these particular (100) planes scatter normally but have their centres displaced relative to the usual positions. The first assumption was adopted by Hoerni and Wooster<sup>37</sup> and the second by Wooster<sup>38</sup> after Lowde<sup>39</sup> had shown that diffuse spikes are revealed by neutron scattering from diamond. Lowde's observations prove that there must be some displacement of atomic centres since neutrons are not affected by the extranuclear electrons. It is possible that a complete explanation will involve both disturbances of the electronic configuration round the anomalous atoms as well as a displacement of the atomic centres. The proposal put forward<sup>38</sup> involves reflection twinning across the (100) plane. It is supposed that there are a number

of such parallel twin planes distributed at random throughout the crystal. The bonds passing from carbon atoms in a twin plane to the neighbours on either side must be coplanar. It seems reasonable to assume that the bonds would tend to be arranged perpendicular to one another and that the atomic planes parallel to the twin plane would be displaced slightly away from it to make this possible. In fig. 3 is shown a normal diamond structure projected on the cube face and in fig. 4 the proposed modification in the neighbourhood of the twin plane. If the unit cell ABCD is supposed normal in all respects except that perpendicular to the twin plane it has expanded from  $a$  to  $a + \delta$ , then we can obtain an idea of the intensity of the spikes by considering the Fourier transform of this cell. Since these cells occur in pairs related by the reflection twin plane we need only consider cosine terms, and write for the transform,  $T$ :

$$T = \sum_{h=1}^4 \cos 2\pi h x \\ = \cos 2\pi h \cdot \frac{1}{4} + \cos 2\pi h \cdot \frac{1}{2} + \cos 2\pi h \cdot \frac{3}{4} + \cos 2\pi h (1 + \delta)$$

For  $h$  having non-integral values very close to 1, 2, 3, 4 this gives a diffuse intensity proportional to  $\cos^2 2\pi h \delta$ . Experimentally it is found that when  $h$  is equal to 3 the intensity of the spikes is very small. Thus to a first approximation we may write;

$$3\delta = \frac{1}{4} \quad \text{or} \quad \delta = \frac{1}{12}$$

If this value were correct the diffuse intensities of the spikes corresponding to the values of  $h$  equal to 1, 2, 3, and 4 would be proportional to 100, 33, 0, and 33 respectively. If  $2\pi\delta$  is put equal to  $28^\circ$  instead of  $30^\circ$  we obtain for this ratio 100:40:1:18. The experimental values are 100:75: < 5: 30. The distance between carbon atoms in the twin plane and their neighbours is 1.72 Å and the angle between bonds on either side of the plane is  $86^\circ$  when  $2\pi\delta$  is put equal to  $28^\circ$ . Thus the agreement between observed and calculated intensities of the spikes is only moderately good and the interatomic distance and bond angles required are quite unorthodox.

#### (b) Anomalous diffuse reflection in white tin

The anomalous diffuse reflection shown by white tin<sup>40</sup> is quite different from that shown by diamond. When the results are represented in reciprocal space they correspond to a diffuse plate arranged so that it passes through the reciprocal point 400 and is normal to the x-axis. A similar plate passes through the reciprocal point 103 and is normal to the z-axis. The thickness of these plates is about one-sixth of the distance between consecutive lattice points along the x and z-axes. A tentative explanation has been advanced based on the fact that at room temperature white tin is close to its  $\alpha - \beta$  transformation point. It is supposed that islands of grey tin can exist in the white tin matrix near to the transformation point and that the strain set up in the lattice due to the differences in cell dimensions of the two forms of tin is responsible for the diffuse reciprocal plates which are observed.

#### Conclusion

Certain general observations concerning the type of investigation described above can now be made. The older static and dynamic methods of determining elastic constants can be applied to polycrystalline materials, whereas the X-ray method cannot. Single crystals which are sufficiently good to afford sharp Laue spots are also good enough for the measurement of elastic constants by the X-ray method.



There is no limitation on the type of crystal which may be studied : it may be metallic, ionic, homopolar or molecular. There is also practically no limitation on size except that very small crystals would require a long exposure. The time taken to collect the data varies with the symmetry of the crystal. A cubic crystal might require some days for its measurement and some further days for its interpretation. Thus, in comparison with some other methods, the X-ray method is slow.

New phenomena are revealed by the X-ray method, e. g. the reciprocal spikes in diamond and the plates in white tin, which could not be found by other methods. These phenomena may be important in understanding the mechanical properties of crystals. It should also be mentioned that the same technique of diffuse X-ray reflections may be used to elucidate the order-disorder problems in alloys. Further, if the investigations are applied to elastic waves of wave-length extending down to twice the side of the unit cell, the complete frequency spectrum of thermally excited elastic waves can be mapped out. There are, therefore, many technical and theoretical problems which can be solved by the use of diffuse X-ray reflections and it is reasonable to expect that the subject will continue to be studied in many parts of the world.

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Fig 1.

Diffuse reflection photograph for a single crystal of lead. L denotes the Laue spot and D the diffuse spot : both L and D correspond to the relp 400. Cu  $K\alpha$  radiation ; radius of camera 5.75 cm.

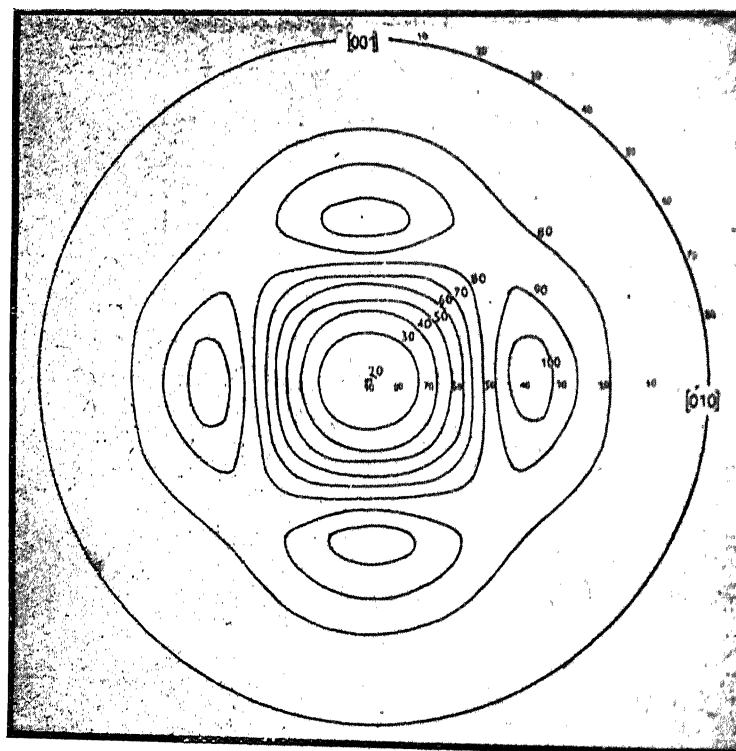
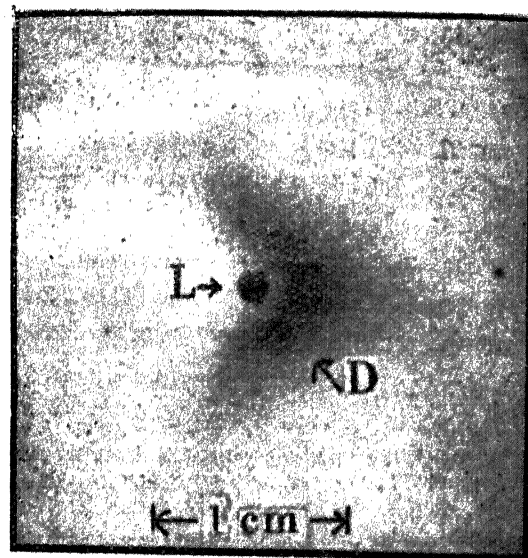


Fig 2.

Stereographic projection of the K-surface for lead associated with the relp 400. The numbers beside the contours are to be multiplied by  $10^{-13}$  to obtain the value of K in  $\text{cm}^2 \cdot \text{dyne}^{-1}$ .

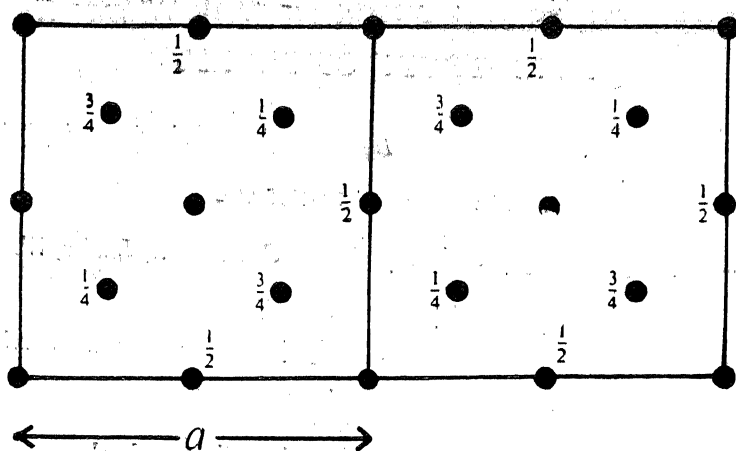


Fig 3.

Projection of the normal structure of diamond on the (001) plane.

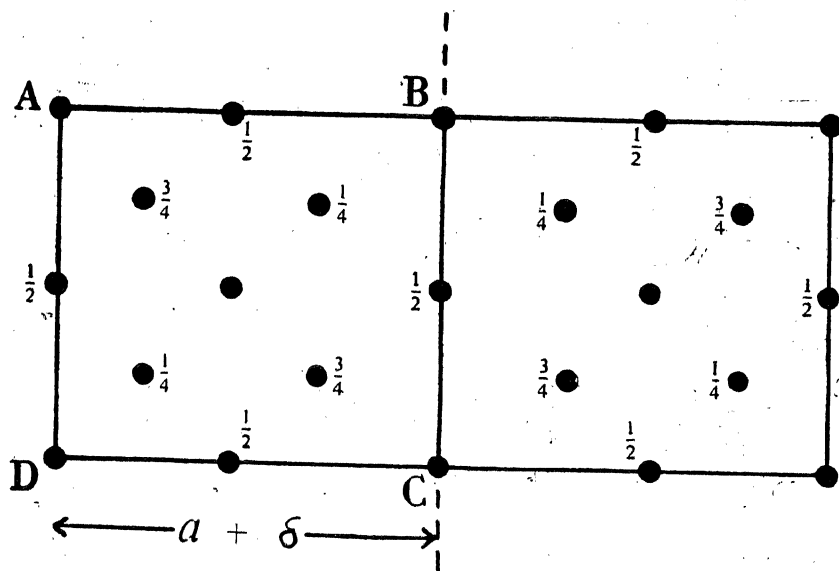


Fig 4.

Projection of the proposed model of the reflection twin. The twin plane is BC and the side AB has increased by  $\delta$  to make the environment of the atoms in the plane BC more nearly a plane square.

# TEMPERATURE DEPENDENCE OF THE DIAMAGNETIC ANISOTROPY OF BENZIL

By

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## ABSTRACT

The diamagnetic anisotropy ( $\chi_{11}-\chi_{\perp}$ ) of benzil crystals changes from 53.3 at 20°C to 57.1 at -134°C (in  $10^{-6}$  c.s.g.c.m.u.). This result is compared with similar data for graphite (21.1 to 29.8) and for urea (no change). There is no change of mean diamagnetism. The question as to whether the change of anisotropy is related wholly or in part to a change of molecular orientation is not yet answered.

An extensive study of the diamagnetic anisotropy of a large number of organic crystals has been made at room temperatures by Krishnan and others (1933, 1935) and by Lonsdale (1938, 1939). The large value of the diamagnetic susceptibility normal to the molecular plane in the case of aromatic compounds has found an explanation in the existence of non-localized  $\pi$  electrons in these molecules. In the case of benzene derivatives, the average effective radius of the spherical orbit of normal valency electrons calculated from susceptibility data is about 0.70 Å. The susceptibility normal to the molecular plane has led to a value of 1.5 to 1.6 Å in single benzene nuclei, about 5.3 Å in the inner phthalocyanine nucleus and about 78 Å in graphite, at room temperature, for the average effective radius of the plane  $\pi$  electron orbits (Lonsdale, 1937). If changes occur in the area of the  $\pi$  electron orbits due to temperature changes, these should be reflected in the magnetic anisotropy. A study was therefore made of the magnetic constants of benzil, at low temperatures, to see whether such changes occur.

The diamagnetic anisotropy of a number of aromatic compounds has been determined at liquid hydrogen temperature by A. Pacault, N. Lumbroso and J. Hoarau (1953). They find an increase in anisotropy ranging from 1% to 8%, which is about the same order as that found in the case of benzil down to -134°C, reported in this paper. The details of the work by A. Pacault and others are given in the thesis of J. Hoarau and N. Lumbroso, which unfortunately we have not yet been able to consult.

## Experimental Details

Measurements of crystal anisotropy were made by the critical torsion method, using 1.3.5 triphenyl benzene as the standard. The low temperature arrangement is shown in Figure 1. The crystal is suspended inside a double-walled glass tube A, of internal diameter 7 mms. placed between the pole-pieces of an electromagnet giving a uniform field of about 4800 oersteds. A continuous current of cold gas

obtained by boiling liquid nitrogen was passed through the walls of the tube A. The temperature inside the tube attained a steady value after fifteen minutes flow of the cold nitrogen. Any desired temperature down to  $-134^{\circ}\text{C}$  could be obtained by regulating the rate of circulation. In order to avoid condensation on the crystal, a glass tube B about 15 cms. long with a narrow mouth of 7 mms. was sealed to the top of A and the entire space in the tubes A and B was dried by passing dry air for half an hour before starting the experiment. Condensation on the outside surface of A was brushed off each time before taking the reading.

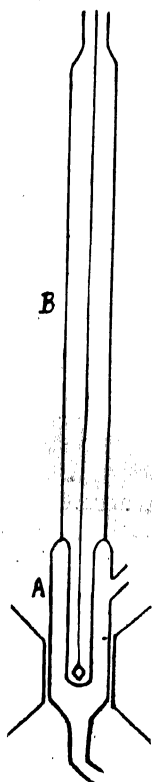


Fig. 1

Measurements of temperature were made by a copper-constantan thermocouple. The temperature of the measuring junction of the thermocouple, corresponding to the observed potential difference between its two junctions, was obtained from the standard calibration table given in the International Critical Tables (1926). The torsion constant of the quartz fibre can be considered to be independent of temperature, since the temperature co-efficient of torsion is negligible. Rubber solution was used as the adhesive at low temperatures.

### Results

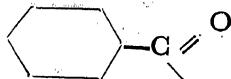
Benzil crystallizes in the trigonal class with  $a=8.42 \text{ \AA}$  and  $c=13.75 \text{ \AA}$ . The space group is  $P3_12$  or  $P3_22$ , with three molecules per unit cell. The mean of several measurements gave for the anisotropy of benzil at room temperature

$\chi_{11}-\chi_1=53.3 \times 10^{-6}$  c.g.s.e.m.u., where  $\chi_{11}$  and  $\chi_1$  are along and normal to the  $c$  axis, respectively.

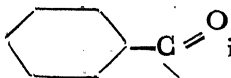
The mean susceptibility estimated from Pascal's data is  $-112.8 \times 10^{-6}$  c.g.s.e.m.u.

Therefore  $\chi_{11}=-130.6 \times 10^{-6}$  c.g.s.e.m.u.

$\chi_1=-77.2 \times 10^{-6}$  " "

The molecule consists of two plane units  inclined at an

angle of about  $97.5^{\circ}$  to each other,\* the whole possessing a diad axis normal to  $c$ . From the known susceptibility values for the benzene ring a reasonable estimate of the three principal molecular susceptibilities  $K_L$ ,  $K_M$  and  $K_N$  can be made. The principal susceptibilities of benzene are  $K_1=K_2=-32.5 \times 10^{-6}$  and  $K_3=-94.3 \times 10^{-6}$  c. g. s. e. m. u. (Lonsdale 1937). The mean susceptibility of benzene  $=-53.1 \times 10^{-6}$  and the mean susceptibility of benzil  $=-112.8 \times 10^{-6}$ . The change in susceptibility due to the replacement of two hydrogen atoms by  $\text{C}=\text{O}$  groups is given by  $-6.6 \times 10^{-6}$ . Therefore the replacement of one hydrogen atom by the  $\text{C}=\text{O}$  group is equivalent to  $-3.3 \times 10^{-6}$ . Assuming that this change is the same in all the directions, the principal susceptibility perpendicular to the molecular

unit  is equal to

\* (Unpublished data kindly provided by Dr. R. Sadanaga).

$K_L = -(94.3 + 3.3) = -97.6 (\times 10^{-6})$  and those in the plane along  $C_1C_4$  and along a line perpendicular to  $C_1C_4$  are given by  $K_M = K_N = (-32.5 + 3.3) = -35.8 (\times 10^{-6})$ .

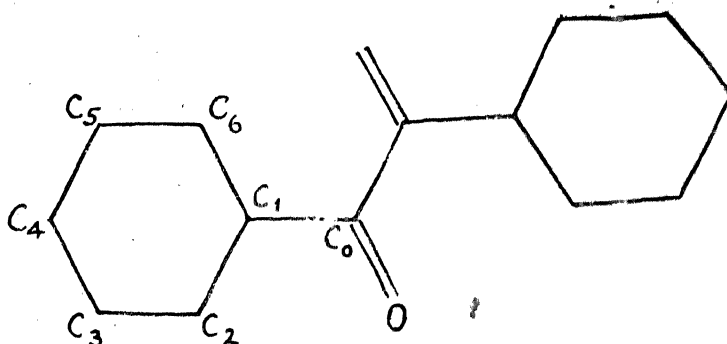


Fig 2.

The theory relating the magnetic constants of a crystal to its structure has been fully developed by Lonsdale and Krishnan (1936) for all crystallographic systems. The molecular susceptibilities  $K_1$ ,  $K_2$  and  $K_3$  are added tensorially to give  $\chi_a$ ,  $\chi_b$  and  $\chi_c$

$$\chi_a = \sum K_1 a_1^2 + \sum K_2 a_2^2 + \sum K_3 a_3^2$$

$$\chi_b = \sum K_1 \beta_1^2 + \sum K_2 \beta_2^2 + \sum K_3 \beta_3^2$$

$$\chi_c = \sum K_1 \gamma_1^2 + \sum K_2 \gamma_2^2 + \sum K_3 \gamma_3^2$$

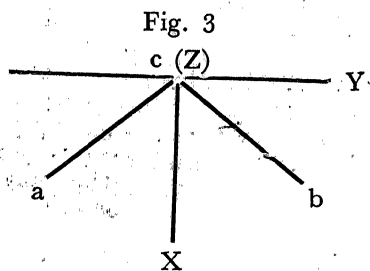
where  $a_1$ ,  $\beta_1$ ,  $\gamma_1$ ,  $a_2$ ,  $\beta_2$ ,  $\gamma_2$  etc., are the direction cosines of  $K_1$ ,  $K_2$  and  $K_3$  with respect to  $\chi_a$ ,  $\chi_b$  and  $\chi_c$ . The summation is taken over all the independently orientated molecules.

The fractional co-ordinates of the atoms at room temperature relative to **a**, **b** and **c** axes are given below\*

	x	y	z
C <sub>0</sub>	·227	·199	·053
C <sub>1</sub>	·229	·026	·075
C <sub>2</sub>	·265	·003	·171
C <sub>3</sub>	·267	—·165	·200
C <sub>4</sub>	·233	—·293	·129
C <sub>5</sub>	·197	—·267	·032
C <sub>6</sub>	·195	—·106	·004
O	·256	·309	·116

\* (Unpublished data kindly provided by Dr. R. Sadanaga).

From these values of the atomic co-ordinates, the directioncosines of  $\vec{K}_L$ ,  $\vec{K}_M$  and  $\vec{K}_N$  with respect to the orthogonal set of axes X, Y and Z (Figure 3) can be calculated. These are given in the table below.



	X	Y	Z
$K_L$	.825	-.528	-.205
$K_M$	.473	.840	-.265
$(C_1 - C_4)$			
$K_N$	.312	.121	0.941

In the case of uniaxial crystals one of the principal crystal susceptibility directions coincides with the crystallographic axis.

Therefore  $\chi_c$  calculated =  $-38.3 \times 10^{-6}$  c. g. s. e. m. u. This calculated value of  $\chi_c$  agrees well with the experimentally determined value  $\chi_c$  (obs) =  $-38.6 \times 10^{-6}$  c. g. s. e. m. u. The low temperature measurements were made on three different crystals of benzil and the results are given in Table I below.

TABLE I

CRYSTAL I		CRYSTAL II		CRYSTAL III	
Temp.	$(\chi_{11} - \chi_1)10^6$	Temp.	$(\chi_{11} - \chi_1)10^6$	Temp.	$(\chi_{11} - \chi_1)10^6$
21.5°C	53.3 <sub>0</sub>	22.5°C	53.4 <sub>6</sub>	22.5°C	53.4 <sub>0</sub>
-51°C	55.5 <sub>4</sub>	-51°C	55.1 <sub>4</sub>	-51°C	55.2 <sub>7</sub>
-108.0°C	56.8 <sub>0</sub>	-93°C	55.9 <sub>7</sub>	-93°C	56.1 <sub>9</sub>
-118°C	56.9 <sub>4</sub>	-108°C	56.2 <sub>0</sub>	-108°C	56.3 <sub>0</sub>
-126°C	57.1 <sub>2</sub>	-126°C	56.5 <sub>0</sub>	-126°C	56.6 <sub>0</sub>
-134°C	57.1 <sub>4</sub>	-134°C	56.5 <sub>5</sub>	-134°C	56.6 <sub>0</sub>

The values of  $\chi_{11} - \chi_1$  are plotted in Figure 4, for crystal I, for which measurements were made with the temperature both decreasing and then increasing again to room temperature. The results for crystals II and III which show a slightly smaller increase give some idea of the repeatability of the effect. At -130°C the curve tends to flatten, showing that it may not increase much at still lower temperatures. Tests made on a powder with the Gouy balance showed that the absolute value of the mean susceptibility remains the same and does not vary with temperature.



Hence the above observed change in susceptibility is more likely to be due to a change in the orientation of the molecule than to a change in the area of the  $\pi$  electron orbits in the benzene ring. The plane molecules of aromatic substances vibrate in the crystal more strongly normal to their plane than parallel to it. This is particularly marked for graphite, for which Krishnan and Ganguli (1939) found a large increase in the diamagnetic anisotropy as the temperature was lowered. We have found a slightly larger increase in the case of graphite,  $(\chi_{11} - \chi_1)$  increasing from  $21.1_4 \times 10^{-6}$  at room temperature to  $29.7_9 \times 10^{-6}$  at  $-133^\circ\text{C}$ . There are markedly anisotropic thermal vibration effects in the case of benzil (Lonsdale and Smith, 1941), but the nature of these is not fully understood. Moreover, as the co-ordinates of the atoms at low temperatures are not yet known, it cannot be said at this stage whether the anisotropy change is related to the large thermal vibration effect in benzil or to a change of molecular orientation.

Urea is of particular interest in this connection, as its anisotropy does not vary over the whole range of temperature examined. The mean of several measurements for the magnetic anisotropy of urea gives  $\chi_{11} - \chi_1 = 2.56 \times 10^{-6}$  c. g. s. e. m. u. The mean susceptibility of urea has been determined by Pascal (1912), Devoto (1932) and Clow (1937). Their values agree closely,  $-33.6_0 \times 10^{-6}$ ,  $-33.4_0 \times 10^{-6}$  and  $-33.6_8 \times 10^{-6}$ , giving a mean value of  $-33.5_8 \times 10^{-6}$ . This gives  $\chi_{11} = -31.8_8 \times 10^{-6}$  and  $\chi_1 = -34.4 \times 10^{-6}$ . Urea crystallises in the space-group  $P4_2/m$  and the unit cell contains two molecules. The planes of the flat molecules are (110) and (110) and remain so at all temperatures from 90K up to the melting point and therefore no change in anisotropy can be expected at low temperatures in respect of molecular re-orientation.

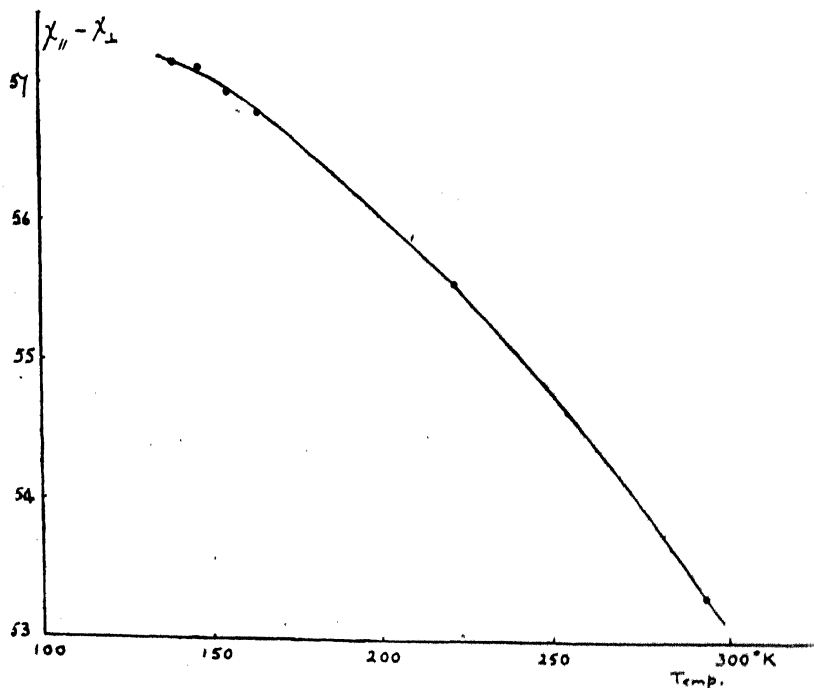


Fig. 4

The molecular anisotropy in the case of urea is in any case small, as would be expected, relative to that of benzene. The fact that it does not change implies

that there is little or no change in the state of resonance of the molecule, although there are marked changes in the thermal vibration of the molecule as the temperature is lowered, the root mean square amplitude of the [100] vibration of the N atom normal to the molecular plane, for example, varying from 0.31 Å at room temperatures down to 0.16 Å at 90°K\*

Krishnan and Ganguli (1941) have shown that the free electron diamagnetism of graphite per carbon atom is equal to the Landau diamagnetism per electron of a free electron-gas obeying Fermi-Dirac statistics and having a degeneracy temperature of 520°K. But it is also not unlikely that the temperature dependence of diamagnetic anisotropy in graphite is related to its abnormally large thermal vibration effect normal to the basal plane (Lonsdale, 1942). The amplitudes of thermal vibration are directly linked with the co-efficients of thermal expansion. Graphite has a co-efficient of expansion along the principal direction, so large, that there is "Poisson" contraction in the direction at right angles. Only at temperatures above 400°C do the thermal vibrations in the layer planes become large enough for the normal to the principal axis to assume a positive value. But in the case of benzil, the increase in anisotropy with decrease of temperature, which is very small in comparison with that of graphite, could be brought about by a slight change in orientation of the molecule, or it could be related to a certain extent to a change in the large anisotropic thermal vibration effect, although this is less likely.

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\* (Data provided by Lonsdale prior to publication elsewhere.)

# PHASE TRANSITIONS IN CRYSTALS COMPOSED OF ORGANIC MOLECULES WITH METHYL GROUPS AT THE MOLECULAR PERIPHERIES

By

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## INTRODUCTION

The molecules having methyl groups at their peripheries are bound together mainly through the Van der Waals forces in the crystalline state. The force is generally so weak that the crystals exhibit polymorphism with slight differences in the free energy which is due to small changes of orientation of methyl groups.<sup>1</sup> Here are a few examples of this sort which interested the authors as to the mechanism of phase transitions. The cases of beryllium oxyacetate  $\text{Be}_4\text{O}(\text{CH}_3\text{CO}_2)_6$ , barium dicalcium propionate  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  and hexamethylbenzene  $\text{C}_6(\text{CH}_3)_6$  provide interesting display of various types of such transitions. The studies on the former two compounds were reported elsewhere.<sup>2,3</sup>

Huffman and his coworkers<sup>4</sup> reported the heat capacity measurements of hexamethylbenzene at  $10^\circ$  intervals from  $90^\circ\text{K}$  to the melting point  $438^\circ\text{K}$ . They found anomalies at  $110^\circ\text{K}$ ,  $135^\circ$ — $165^\circ\text{K}$ , and  $383^\circ\text{K}$  (see Fig 1). Pauling<sup>5</sup> suggested that the transition at  $110^\circ\text{K}$  would mark the onset of the rotation of methyl groups around the C-C side bonds. The proton nuclear magnetic resonance experiments,<sup>6</sup> however, seem to exclude this possibility as Andrew showed that the observed second moment  $13.0 \text{ gauss}^2$  at  $95^\circ\text{K}$  corresponds to the rotating  $\text{CH}_3$  group scheme and that the second moment  $2.5 \text{ gauss}^2$  above  $210^\circ\text{K}$  has to be accounted for by the rotational oscillation of the whole molecule round its hexagonal axis. This explanation, on the other hand, results in the hazards in the assignment of the  $383^\circ\text{K}$  transition which accompanies a change of crystal structure. The extraordinary behavior above  $383^\circ\text{K}$  as to its volume change<sup>7</sup> also remains unexplained. In view of these recent informations obtained, it was considered of value to carry out the continuous measurements of the heat capacity of hexamethylbenzene particularly above the room temperature.

## EXPERIMENTAL

Hexamethylbenzene crystallized from benzene solution was further purified by fractional sublimation in vacuo until the constant melting point is obtained, m. p.  $165.3^\circ\text{C}$ . The apparatus for the measurement of the heat capacity is the conduction calorimeter which was fully described elsewhere.<sup>8</sup>

## RESULTS

The results are given in Fig. 1 and in Table 1. The magnitude of the anomaly around  $95^\circ\text{C}$  gets smaller and smaller in the repeated runs, with no indication of its presence in the cooling experiments. Corresponding to the

maximum of the volume-temperature curve (Fig. 2), there is a discernible maximum around 135°C, though the effect is seen much pronounced in the volume change.

TABLE 1  
*Heat capacities of Hexamethylbenzene*

t°C	C <sub>p</sub> $\frac{\text{cal.}}{\text{mole.}}$	t°C	C <sub>p</sub> $\frac{\text{cal.}}{\text{mole.}}$
0.0	57.84	107.45	82.46
5.25	58.55	transition	
10.52	59.29		
15.59	60.22	114.00	75.75
20.66	61.20	118.38	76.14
28.24	62.70	120.55	76.45
35.65	64.08	124.91	77.06
43.00	65.64	129.15	77.31
47.80	66.66	131.25	77.33
55.04	68.01	133.34	77.19
59.81	68.44	135.48	77.02
64.49	69.19	137.60	76.98
71.55	70.86	139.66	76.72
78.43	72.05	141.72	76.90
85.22	72.84	147.90	77.91
89.73	74.59	152.05	82.06
94.25	75.75	156.18	84.31
96.40	77.70	160.30	96.86
98.52	77.10	fusion	
100.85	79.40		
105.24	81.10		
		166.38	87.19
		168.40	82.96
		170.42	81.71

Table 2 lists the quantities measured at the transition and the melting points.

TABLE 2

	temperature	enthalpy change	entropy change
transition	... 110.4°C	440 cal./mole	1.15 cal./mole. deg.
fusion	... 165.2°C	4920 cal./mole	11.2 cal./mole. deg.

## DISCUSSION

The heat capacity curve of  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  is reproduced in Fig. 3 for the sake of reference. A comparison of this with the transition of hexamethylbenzene at  $110^\circ\text{C}$ . leads one to assume that the mechanism of these transitions would be similar to each other. The difference in the shape of curves is that one of the peaks in  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  at the lower temperature side is flattened to give a terrace in the case of hexamethylbenzene. We find a close relationship in the crystal structures of the two compounds on the basis of the intermolecular configuration of methyl groups.

As illustrated in Fig. 4 schematically, the six methyl radicals belonging to six different propionate ions meet nearly hexahedrally. Below the transition point, these methyl radicals are considered to be fixed in definite orientations and as shown in Fig. 5 one of the oppositely situated methyl group pairs may have a little greater methyl-to-methyl distance than the other two pairs in order to satisfy the tetragonal or the orthorhombic symmetry.\* The rotational oscillation [of the methyl groups] around the  $\text{C}(\alpha)\text{-C}(\text{carboxyl})$  bond will become gradually violent as the temperature rises, which causes a synchronous, in-phase, movement of the two pairs of methyl groups just like a meshed bevel gear system. The remaining pair of methyl radicals can not come into coupling with the gear system until the thermal expansion permits the loosening of meshing. The further enhancement of the thermal motion thus has to bring the six methyl radicals to equivalence, changing the crystal symmetry to the cubic.

Quite an analogous situation occurs in hexamethylbenzene. The nearly hexagonal arrangement of the molecules in the low temperature modification<sup>9</sup> (Fig. 6) forms a meshed spur gear systems as illustrated in Fig. 7 in which one third of molecules in a layer cannot couple with the gear system by the same reasoning as for  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ .<sup>6</sup> The difference between these two compounds will be clear if one considers the number of possible configurations (in the momentum space) in the two cases.

There are  $N$  separate gear systems in a  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  crystal containing  $N$  formula units. The total number of possible configurations is therefore  $n_1^N$ , if  $n_1$  be the number of configurations within a separate set of six methyl radicals.† On the other hand, a whole (001) layer of hexamethylbenzene forms a set of gears with the number of possible configurations  $n_2$ , and thus the total number of configurations will be  $N \frac{n_2}{3}$  of the order of  $n_2$ , since the number of layers in a block of crystal is of the order of  $N^{\frac{1}{3}}$ ,  $N$  being again the number of molecules in the block. The extent, to

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\* The precise crystal structure of the low temperature phase of  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  is not known, but it is of lower symmetry than the cubic system to which the high temperature modification belongs. This was evidenced by an optical observation. See ref. (3).

† There are three ways in which an uncoupled pair of oppositely situated methyl groups is taken out of three pairs and there are two types of meshing for each of these ways, clockwise and counter-clockwise revolutions. [Here, as a first approximation, the possible correlation between the motions of  $\text{C} \begin{smallmatrix} \nearrow 0 \\ \searrow 0 \end{smallmatrix}$  and  $\text{CH}_3$  groups is ignored]

which the motion of methyl radicals belonging to different molecules is in cooperation, will be very much greater in  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$  than in hexamethylbenzene. This tentative interpretation may correspond to the different heat capacity curves, one with a peak and the other only with a flattened terrace.

The anomalous behavior in the volume expansion is quite hard to explain. If we extrapolate the room temperature portion of the  $V$ - $T$  curve in Fig. 2, we obtain perfectly normal behavior which a hydrocarbon would show (dotted line). The excess volume change above this dotted line is thus to be regarded as abnormal from such a point of view; the transition is taking place gradually between about 60° and 165°C rather than only at 110°C. The broad maximum of the heat capacity curve between 110° and the melting point will be possibly due to the relatively large work associated with the anomalous volume change, although this must be ascertained by determining the heat capacity at constant volume. Therefore it may be assumed that there is no appreciable change in the number of degrees of freedom of motion between 110°C and the melting point. The sum 12.3 cal./mole. deg. of entropies of transition and of fusion is to be compared with the entropy of fusion 13.1 e.u. of naphthalene, in accord with the Walden's rule. When liquid naphthalene, solidifies, all the rotational degrees of freedom are considered to freeze as it has no transitions in the solid state. It will be safely assumed that a little smaller entropy of melting of hexamethylbenzene is related to the excitation of orientational degrees of freedom around the molecular axes perpendicular to the hexagonal axis and, at the same time, to the formation of holes in liquid.\* The X-ray evidence shows that the expansion and contraction in question occur only within the (001) layer, the axial ratio  $b/a$  as well as the parameter  $c$  being constant (see Table 3, Fig. 8). The remaining possibilities would then be some change of relative arrangement of molecules in the (001) layer. If the methyl radicals can mesh geometrically with each other between neighboring molecules, the volume per molecule would diminish to some extent; this can be achieved by turning all the molecules around the hexagonal axis by 30°, assisted by the enhanced rotational oscillation around this axis.

TABLE 3

*Powder Photographic Data at Various Temperatures.*<sup>10</sup>

Temperature (°C)	...	115°	130°	155°
a	...	9.13kX	9.36	9.06
b	...	16.12	16.22	15.70
c	...	7.52	7.52	7.52
$b/a$	...	1.77	1.73	1.73
$\rho(\text{X-ray})$	...	0.98	0.94	1.00
$\rho(\text{dilatometry})$	...	0.94	0.91	0.97

This view may be supported partly by the decreasing interaction between (inter-layer) methyl groups (the distance increases by contraction) and partly by the possibility of interpenetration of hydrogen as suggested by Simons and Hickman.<sup>11</sup>

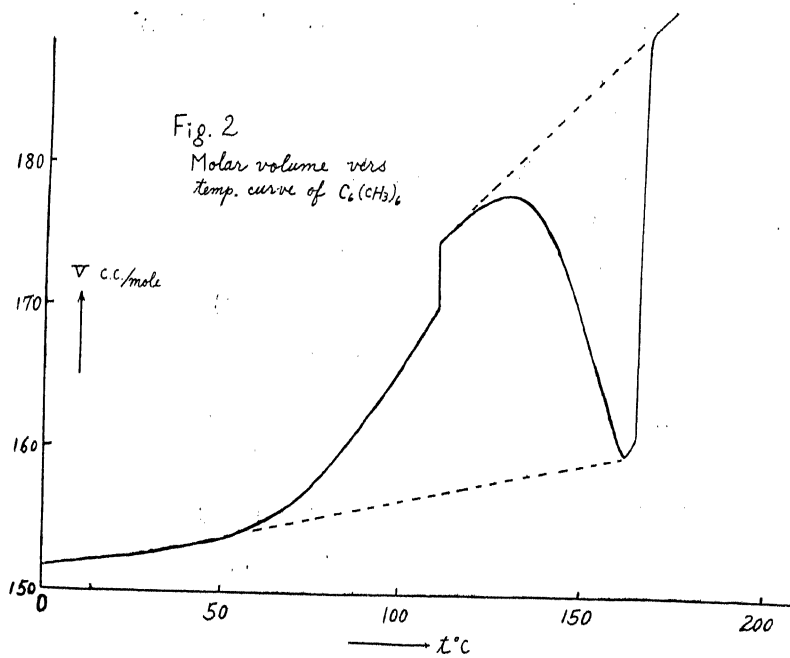
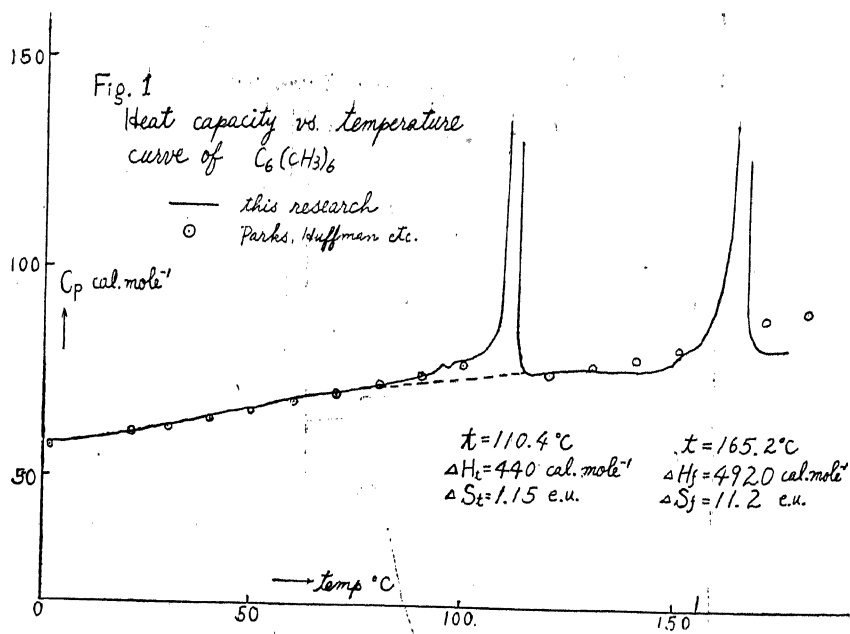
\* It is worthwhile to note here that the hexamethylbenzene crystal is composed of layer lattice just below the melting point, whereas all the other polynuclear aromatic compounds show no layer structures.

Another factor which should be considered is the disappearance of lattice vacancies due to thermal agitation which, however, is contrary to the general change of equilibrium concentration of lattice vacancies with temperature.

In order to elucidate the mechanism of such peculiar transition further, the information concerning the temperature dependences of the depolarization factor of Raman lines, the diamagnetic anisotropy would be highly desirable.

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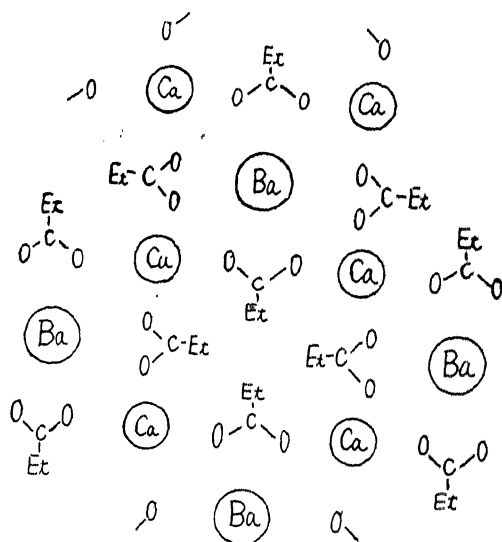
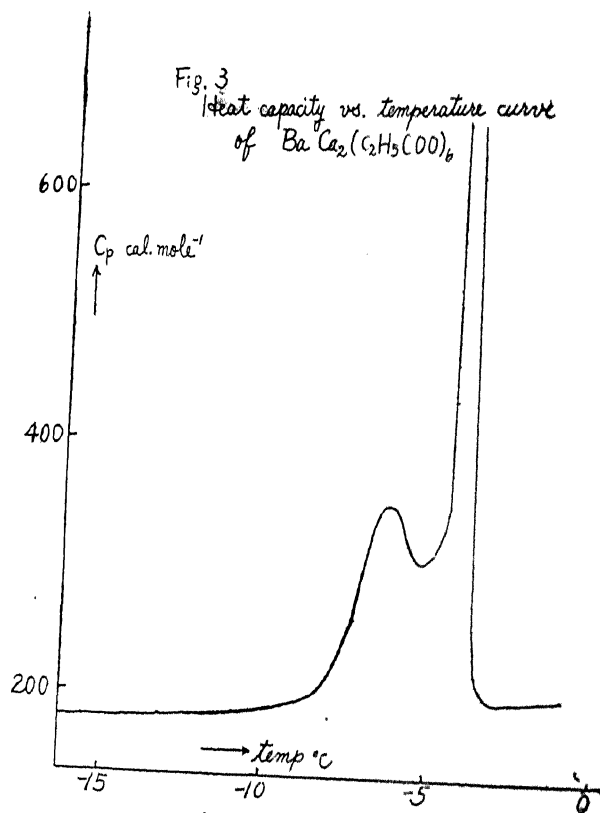


Fig. 4  
Two-dimensional schematic representation of  
relative arrangement of carboxylic  
radicals around metallic ions.

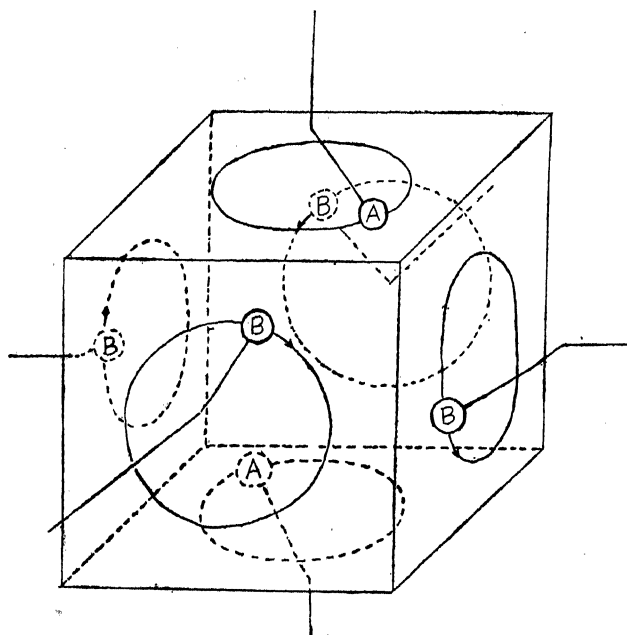


Fig. 5

Schematic illustration of the correlated molecular motion of six methyl groups.

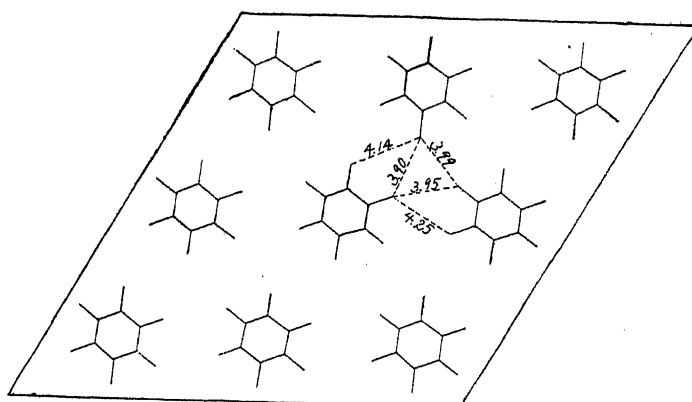


Fig. 6

Low temperature structure of  $C_6(CH_3)_6$



# SCATTERING OF X-RAYS BY DEFECT STRUCTURES

By

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## ABSTRACT

The intensity of X-ray scattering from a crystal containing defects is shown to depend in a simple way on the Fourier transforms of the defects considered separately. Some applications of the theory are mentioned

## 1. Introduction

General theories of the coherent scattering of X-rays by a crystal which is disordered or contains imperfections have been given by Zachariasen (1945), and by Matsubara (1952). The effects of imperfections of a particular kind have often been calculated, for example for 'impurity' atoms (Huang 1947) and for screw dislocations (Wilson 1952). The general theory given here has the same starting-point as that of Matsubara, but is developed in a different way. The results are equivalent to those of Zachariasen, but are more easily applied to particular problems as is shown by some examples.

## 2. General theory

We consider a spherical crystal of radius  $R$ , containing  $N$  unit cells. If we denote the crystal by  $C$ , and its Fourier transforms by  $T_C$ , then

$$T_C(\mathbf{s}) = T_L(\mathbf{s}) F(\mathbf{H}) \quad \dots\dots (1)$$

$\mathbf{s}$  is a vector in reciprocal space,  $\mathbf{H}$  a vector to a point of the reciprocal lattice.  $T_L(\mathbf{s})$  is the transform of a lattice bounded by a sphere, and has thus an appreciable value only within about  $R^{-1}$  of  $\mathbf{s} = \mathbf{H}$ . The transform of one unit cell,  $F(\mathbf{s})$ , which varies comparatively slowly with  $\mathbf{s}$ , thus appears in (1) as  $F(\mathbf{H})$ .

We now imagine a defect  $\Delta$  to be introduced into the crystal to produce an imperfect crystal  $C + \Delta$ . We then have

$$T_{C+\Delta}(\mathbf{s}) = T_C(\mathbf{s}) + T_\Delta(\mathbf{s}) \quad \dots\dots (2)$$

If we now define  $F_M(\mathbf{H})$  as the structure factor of the *average* unit cell of  $C + \Delta$ , it may be shown that

$$F_M(\mathbf{H}) = F(\mathbf{H}) + \frac{1}{N} T_\Delta(\mathbf{H}) \quad \dots\dots (3)$$

We next define  $T_M(\mathbf{s}) = T_L(\mathbf{s}) F_M(\mathbf{H}) \quad \dots\dots (4)$

$T_M(S)$  is thus the transform of a crystal of radius  $R$ , composed of identical average unit cells. Combining (2), (3) and (4) we have

$$T_{C+\Delta}(S) = T_M(S) + \left\{ T_{\Delta}(S) - \frac{1}{N} T_L(S) T_{\Delta}(H) \right\} \dots (5)$$

When the first term on the right is large, the second is zero, and conversely. The intensity from the defective crystal is thus proportional to

$$|T_{C+\Delta}(S)|^2 = |T_M(S)|^2 + \left| \left\{ T_{\Delta}(S) - \frac{1}{N} T_L(S) T_{\Delta}(H) \right\} \right|^2 \dots (6)$$

The first term on the right will be recognised as the Laue-Bragg intensity

$$J_1(S) = |T_M(S)|^2 \dots\dots (7)$$

The second must represent the diffuse intensity, and except within about  $R^{-1}$  of  $S=H$  it can be written as

$$J_2(S) = |T_{\Delta}(S)|^2 \dots\dots (8)$$

We may note from (6) however that as the second term on the right is zero for  $S=H$ , there is no diffuse intensity *exactly* at reciprocal lattice points. This agrees with Zachariasen's (1945) conclusion.

The change of Laue-Bragg intensity can also be expressed in terms of  $T_{\Delta}(S)$ . A short calculation gives the fractional change of intensity in going from  $C$  to  $C+\Delta$  as

$$\frac{|F_M(H)|^2 - |F(H)|^2}{|F(H)|^2} = \frac{1}{N} \left( \frac{T_{\Delta}(H)}{F(H)} + \frac{T_{\Delta}^*(H)}{F^*(H)} \right) + \frac{1}{N^2} \left( \frac{|T_{\Delta}(H)|^2}{|F(H)|^2} \right) \dots (9)$$

The second term on the right will be neglected in subsequent application of this result.

Equation (9) gives the change in *height* of Laue-Bragg maxima,—one can no longer define integrated intensity precisely, since Laue-Bragg and diffuse intensity cannot be separated from one another.

In almost all instances it will be the case that  $\Delta$  can be regarded as arising from the simultaneous presence of a large number of relatively small defects, which may or may not be identical, but are in any case centred on different points in the crystal. If each atom in the crystal is influenced by only one defect, we can take

$$\Delta = \sum_{j=1}^n \delta_j \dots\dots (10)$$

where each  $\delta_j$  is a defect centred in the crystal at a point  $R_j$ , so that

$$T_{\Delta}(S) = \sum_{j=1}^n T_{\delta_j}(S) e^{2\pi i R_j \cdot S} \dots\dots (11)$$

and therefore

$$T_{\Delta}(\mathbf{H}) = \sum_{j=1}^n T_{\delta_j}(\mathbf{H}) \quad \dots \quad (12)$$

Equations (10), (11) and (12) apply exactly, no matter how large the displacement of atoms around a defect may be, provided that the influence of a defect is limited in range, and the concentration of defects small. If the defects consist only in the replacement of atoms, without displacement, the results apply without any restriction. In many interesting cases which occur in practice however, no upper limit can be set to the range of influence of a defect, as is shown by the expansion of the lattice in proportion with the defect concentration. If the effects produced combine linearly, i. e. if the net displacement of any atom is the sum of the displacements that would be produced by each defect  $\delta_j$  acting alone, and if the same is true for the net expansion of the lattice, then it can be shown that Equations (10), (11) and (12) are still approximately true. A necessary condition is that  $\exp 2\pi i \mathbf{t} \cdot \mathbf{S}$  may be taken as  $1 + 2\pi i \mathbf{t} \cdot \mathbf{S}$  to good approximation, so that  $\mathbf{t}$ , the displacement of any atom from the position occupied in the "average" crystal, must be small. In what follows we assume this condition to be satisfied.

Returning now to Equation (12), we substitute the value of  $T_{\Delta}(\mathbf{H})$  given there in Equation (9), and obtained for the fractional change in Laue-Bragg intensity

$$\frac{1}{N} \left\{ \frac{\sum_{j=1}^n T_{\delta_j}(\mathbf{H})}{F(\mathbf{H})} + \frac{\sum_{j=1}^n T_{\delta_j}^*(\mathbf{H})}{F^*(\mathbf{H})} \right\} \quad \dots \quad (13)$$

If all the defects are the same, this is simply

$$\frac{n}{N} \left\{ \frac{T_{\delta}(\mathbf{H})}{F(\mathbf{H})} + \frac{T_{\delta}^*(\mathbf{H})}{F^*(\mathbf{H})} \right\} \quad \dots \quad (14)$$

It is readily shown that when the defects are distributed completely at random, the diffuse intensity is given by

$$J_2(\mathbf{S}) = \sum_{j=1}^n \left| T_{\delta_j}(\mathbf{S}) \right|^2 \quad \dots \quad (15)$$

### 3. Applications of the theory

The results given above have been applied to the problem of the scattering of X-rays by solid solutions. This problem has already been solved by Huang (1947). The simpler treatment outlined here leads to essentially the same conclusions, but is capable of extension to more complicated crystal structures.

Each defect  $\delta$  consists in the replacement of an atom of scattering factor  $f_1$  by another of scattering factor  $f_2$  in a crystal of, for example, copper. Surrounding atoms at  $\mathbf{r}$  are taken to be displaced by  $\frac{C\mathbf{r}}{r^3}$ . The crystal is cubic, of cell side  $a$ .

The details of the calculation will not be reproduced here, but it is found that the fractional change of Laue-Bragg intensity is given by

$$\frac{2n}{N} \left( \left( \frac{f_2}{f_1} - 1 \right) - \frac{4 \cdot 22 \pi^2 c^2 H^2}{(\frac{1}{2}a)^4} \right) \dots \dots (16)$$

Apart from terms involving  $(n/N)^2$ , this result is the same as that given by Huang. An approximate expression for the diffuse intensity around each reciprocal lattice point  $\mathbf{H}$  is

$$n \left[ (f_2 - f_1) - \frac{16 \pi c S f_1}{a^3 |\mathbf{S} - \mathbf{H}|} \cos(\mathbf{S}, \mathbf{S} - \mathbf{H}) \frac{\sin \sqrt{2} \pi a |\mathbf{S} - \mathbf{H}|}{\sqrt{2} \pi a |\mathbf{S} - \mathbf{H}|} \right] \dots \dots (17)$$

Both qualitatively and quantitatively this expression gives results close to those obtained by Huang, the main features being :—

- (a) An increase of diffuse intensity with  $\mathbf{S}$ , (approximately as  $\mathbf{S}^2$ ).
- (b) A concentration of diffuse intensity near  $\mathbf{S} = \mathbf{H}$ , falling off somewhat more rapidly than  $|\mathbf{S} - \mathbf{H}|^{-2}$ .
- (c) Almost zero intensity in a plane passing through each reciprocal lattice point, the normal to the plane being the direction of  $\mathbf{H}$ .

The same general approach can be used to make qualitative predictions about the diffuse intensity from neutron-irradiated crystals of boron carbide. It has been shown by Tucker and Senio (1955) that the defect consists mainly in the removal of the central carbon atom of a chain of three, resulting in an inward movement, predominantly in the  $c$ -direction, of surrounding atoms. On this basis, the theory outlined above predicts a diffuse intensity concentrated around reciprocal lattice points, approximately proportional in magnitude to the intensity of the corresponding Laue-Bragg intensity. The diffuse intensity surrounding (ool) reciprocal lattice points should be particularly strong, but should fall to a low minimum on a plane passing through the point (ool) within normal along  $\mathbf{C}^*$ . Other reciprocal lattice points should show this feature to a lesser extent.

Two possible further applications of the theory are to (a) the calculation of the intensity of scattering from simple crystals (e. g. metallic elements, diamond etc.) containing Frenkel defects, (b) the explanation of the anomalous X-ray reflexions from certain diamond crystals, most recently studied by Hoerni and Wooster (1955). Some progress has been made with both these problems.

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# DETERMINATION OF ELASTIC CONSTANTS FROM THE STUDIES OF THE THERMAL DIFFUSE X-RAY SCATTERING OF SINGLE CRYSTALS BY THE PHOTOGRAPHIC METHOD

(THE CASE OF HEXAGONAL CRYSTALS BELONGING TO  $D_3$  CLASS)

By

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(Communicated by Prof. K. Banerjee)

Read at the Silver Jubilee Session on 27th December 1955 at the University of Lucknow

## ABSTRACT

According to the thermal theories of diffuse X-ray reflexions, the elastic constants of a crystal can be determined from the intensities of the diffuse reflexions. The special types of reflexions and the particular direction of the thermal wave vectors which may conveniently be used for such determinations in the case of hexagonal crystals belonging to the  $D_3$  group have been discussed. The advantages of the photographic method have also been indicated. The results of such measurements with benzil single crystals are given. The ratios of the elastic constants determined are  $C_{11}/C_{66}=2.81$  and  $C_{11}/C_{44}=1.54$ .

The determination of the elastic constants of small crystals from measurements of strains produced by mechanical means is very difficult and in many cases impossible. For this reason very few measurements have been carried out on organic crystals which are generally small in dimensions. Recently the possibility of measuring the elastic constants of crystals from the intensities of thermal diffuse X-ray reflexions have been demonstrated by Ramchandran & Wooster (1951) and they have actually determined the values of the elastic constants of a number of cubic inorganic crystals and hexamethylene-tetramine by a Geiger-Counter X-ray spectrometer. In this method the divergence of the incident beam and the scattered beam received by the counter were large and a divergence correction had to be applied to the measured intensities. This correction is very laborious and complicated.

In the photographic method a very small area of the reflexions are covered by the photometric scanning spot of light and hence the divergence of the scattered beam in this case is negligible. As the crystal generally used in this method are small, the effective divergence of the incident beam is also very small. In this method, therefore, there is no necessity of applying the divergence correction. The experimental arrangements as usual consists of allowing a beam of monochromatised X-rays to fall on a crystal set at a desired orientation on the axis of a camera and taking a Laue photograph. The indices of the planes giving rise to the diffuse reflexions are ascertained in the manner indicated by Lonsdale & Smith (1941) and Ganguly (1942). Intensities of these reflexions corresponding to different angles of deviation are computed from the photometric measurements along particular directions Sen (1953). From these intensity values and the values of the thermal wave vectors deduced from the known orientations the elastic constants are evaluated.



According to Born (1942-43), the intensity  $I_s$  scattered by a thermally vibrating crystal of volume  $\delta v$  in the direction  $\phi$  is given by the relation,

$$I_s = I_e N K T F^2 \cdot d(q)/m$$

$$= I_e K T F^2 \cdot \frac{\delta v}{V} \cdot \frac{d(q)}{m}, \text{ for very long thermal waves ;}$$

where  $I_e$  is the intensity scattered by a free electron under the conditions of the experiment

$N$  is the no. of unit cells in the vol.  $\delta v$ ,

$V$  is the volume of the unit cell,

$T$  is the temperature in the absolute scale,

$K$  is the Boltzman constant

$F$  is the structure factor of the plane concerned,

$m$  is the mass of the unit cell

$$\& d(q) = \sum_{\alpha\beta} D^{-1}(q) X_{\alpha}^{(h)} X_{\beta}^{(h)}$$

in which  $D^{-1}(q) = \text{adj } D(q) / \det D(q)$  are the elements of the matrix inverse to the matrix  $D(q)$ .

The elements of the matrix  $D(q)$  are given by,

$$\rho D_{11}(q) = C_{11}q_1^2 + C_{66}q_2^2 + C_{55}q_3^2 + 2C_{65}q_2q_3 + 2C_{16}q_1q_2 + 2C_{15}q_1q_3$$

$$\rho D_{22}(q) = C_{66}q_1^2 + C_{22}q_2^2 + C_{44}q_3^2 + 2C_{24}q_2q_3 + 2C_{46}q_1q_2 + 2C_{26}q_1q_3$$

$$\rho D_{33}(q) = C_{55}q_1^2 + C_{44}q_2^2 + C_{33}q_3^2 + 2C_{43}q_2q_3 + 2C_{36}q_1q_2 + 2C_{46}q_1q_3$$

$$\rho D_{23}(q) = C_{66}q_1^2 + C_{24}q_2^2 + C_{43}q_3^2 + (C_{13} + C_{44})q_2q_3 + (C_{46} + C_{36})q_1q_2 + (C_{46} + C_{16})q_1q_3$$

$$\rho D_{31}(q) = C_{16}q_1^2 + C_{46}q_2^2 + C_{36}q_3^2 + (C_{46} + C_{36})q_2q_3 + (C_{16} + C_{56})q_1q_2 + (C_{56} + C_{11})q_1q_3$$

$$\rho D_{13}(q) = C_{16}q_1^2 + C_{26}q_2^2 + C_{45}q_3^2 + (C_{46} + C_{16})q_2q_3 + (C_{56} + C_{14})q_1q_2 + (C_{12} + C_{66})q_1q_3$$

$q_1, q_2, q_3$  being the components of the wave vector  $q$  (i.e. the vector joining the point of observation in the reciprocal lattice to nearest node along the three axes of reference used in crystal elasticity,  $X_{\alpha}^{(h)}$  &  $X_{\beta}^{(h)}$  are the components of the reciprocal lattice vector corresponding to the node along the same axes,  $\rho$  is the density of the crystal and  $C_{rs}$  are the elastic constants (stiffness coefficients). For hexagonal crystals belonging to  $D_3$  class,

$C_{12} \neq 0$ ,  $C_{33} \neq 0$ ,  $C_{22} = C_{11}$ ,  $C_{55} = C_{44}$ ,  $C_{66} = C_{14}$ ,  $C_{24} = -C_{14}$  &  $C_{23} = C_{13}$  and all other constant vanish.

For the  $(h\ 0\ 0)$  reflexions for the reciprocal lattice points lying in the plane normal to  $[00\ 1]$  and on the normal to the reciprocal lattice vector corresponding to this node,

$$d(q) = \frac{\rho}{q^2} \cdot \frac{|X^{(h)}|^2}{C_{66}}, \text{ Since } q_1 = q_2 = 0 \text{ in this case.}$$

Similarly for (h 0 0) nodes for points lying on the reciprocal lattice vector corresponding to the node,  $\bar{q}_1 = \bar{q}_2 = 0$  and

$$d(\bar{q}) = \frac{\rho}{\bar{q}_1^2} \cdot \frac{|\bar{X}^{(h)}|^2}{C_{11}}$$

Thus the ratios of the observed intensities  $I_{20}$  &  $I_{01}$  of a (h0.0) diffuse reflexion in a particular photograph at the angles corresponding to the points of intersection of the sphere of reflexion with the directions normal to and along the reciprocal lattice vector through this node in the plane normal to  $[00\cdot1]$ , give the ratio of the elastic constants  $C_{11}$  and  $C_{66} = \frac{1}{2}(C_{11} - C_{12})$ . For

$$\frac{I_{20}}{I_{01}} = \frac{(1 + \cos^2 \chi_2)}{(1 + \cos^2 \chi_1)} \cdot \frac{\bar{q}_1^2}{\bar{q}_2^2} \cdot \frac{C_{11}}{C_{66}}$$

where  $\chi$  is the angle of deviation corresponding to the directions of observation and in this expression all other quantities except  $C_{11}/C_{66}$  are known. Again for (h0.0) reflexions for points lying on the direction through this node parallel to  $[00\cdot1]$ ,  $\bar{q}_1 = \bar{q}_2 = 0$  and

$$d(\bar{q}) = \frac{\rho}{\bar{q}_3^2} \cdot \frac{|\bar{X}^{(h)}|^2}{C_{44}}$$

Hence from the ratios of the intensities of a (h 0.0) diffuse reflexion observed in a particular photograph at the angles corresponding to the points lying on the reciprocal lattice vector through (h 0.0) node concerned and on the direction parallel to  $[00\cdot1]$  through this node, the ratio  $C_{11}/C_{44}$  can be determined. For (h 0.1) reflexions for points lying on the direction through this node parallel to  $[00\cdot1]$

$$d(\bar{q}) = \frac{\rho}{\bar{q}_3^2} \cdot \frac{|\bar{X}^{(h)}|^2}{\left\{ \frac{L^2}{C_{44}} + \frac{N^2}{C_{33}} \right\}}$$

where L, M & N are the direction cosines of  $\bar{X}^{(h)}$ . Hence from the ratio of the intensities of diffuse reflexions of a (h 0.1) reflexion and a (h0.0) reflexion observed in the same photograph (or converted to the same relative scale) corresponding to the points lying on a line parallel to  $[00\cdot1]$  through the respective nodes, the ratio  $C_{44}/C_{33}$  can be obtained. For the points lying in the reciprocal lattice plane through a (h 0.0) node normal to the reciprocal lattice vector corresponding to this node,  $\bar{q}_1 = 0$  &  $\bar{q}_2 = \bar{q}_3 \neq 0$  and

$$d(\bar{q}) = \frac{\rho}{C_{66} \bar{q}_2^2 + C_{44} \bar{q}_3^2 + 2C_{11} \bar{q}_2 \bar{q}_3} \cdot \frac{|\bar{X}^{(h)}|^2}{C_{11}}$$

Hence from the observed intensities of a (h 0.0) reflexion for such points and for the points lying on the reciprocal lattice vector corresponding to this node the ratio  $C_{11}/C_{44}$  can be evaluated, as the ratios  $C_{11}/C_{66}$  and  $C_{11}/C_{44}$  are already known.

The ratios of the elastic constants can be very accurately determined in the following manner. The intensities of the diffuse reflexions in the different photographs are reduced to relative values corresponding to the same intensity of the incident beam by the use of a calibrator. A very convenient method is to dust a small amount of aluminium powder on the crystal thereby recording in the Laue photographs a number of aluminium powder diffraction lines. Since the same amount of the powder is bathed in the beam for the set of photographs taken with one crystal mounted with a particular axis coinciding with the vertical axis of the camera, the intensities of the aluminium powder diffraction lines may be used as calibration lines. The relative intensities of diffuse reflexions thus obtained from a

number of photographs corresponding to points lying on a particular radial direction through a particular node are plotted against the square of the reciprocal of the thermal wave vectors. The curves thus obtained are straight lines passing through the origin when the intensities are corrected for Compton scattering, scattering due to  $\lambda/2$  etc. The ratios of the slopes of such curves for different directions and different reciprocal lattice nodes give the ratios of elastic constants as indicated above. The absolute values of the elastic constants can be determined if the intensity of the incident beam is known. The accurate measurement of both the incident and diffuse reflexions from each photograph is difficult as the incident beam is roughly  $10^6$  to  $10^7$  times as intense as the diffuse reflexions. In the photographic method this measurement can be effected by absorbing the direct beam by a Ni or Cu foil of known thickness and recording the absorbed direct beam on the same film throughout the whole exposure. Though the error in measuring the incident beam is larger, in this method the observation can be carried out for points having very low  $q$  values which is a necessary condition for applying the above theory. Thus the accuracy of the values determined by this method for polyatomic structures are more than those obtained by the Geiger-counter spectrometer. In the ultrasonic wave method it is very often difficult to assign the correct node of vibration on which the values depend.

Some of the ratios of the elastic constants of benzil, belonging to  $D_2$  class of hexagonal system, determined from the diffuse X-ray reflexions by the photographic method are detailed in the table given below.

**Table giving the elastic constants of benzil**

Reciprocal lattice node considered—(40·0)

Crystal Structure factor of the (40·0) reflexion—51

Axial lengths of the crystal -  $a=8.38\text{\AA}$ ,  $C=13.78\text{\AA}$ .

Orientation of the crystal		Thermal wave vector $q$	Direction of $q$	Angle of deviation	Relative intensity value	Ratio of the elastic constants determined
Crystal axis coinciding with the vertical axis of the camera	Direction of the Incident beam					
[00·1]	Incident beam making $4^\circ 6'$ with [10·0]	$1.6 \times 10^6 \text{ cm}^{-1}$	Along the vector corresponding to the node	$51^\circ 48'$	0.80	} $C_{11}/C_{66} = 2.80$
"	"	$0.75 \times 10^6 \text{ cm}^{-1}$	Normal to [00·1] and the vector corresponding to the node	$50^\circ 15'$	10.40	

Orientation of the crystal		Thermal waver vector $\bar{q}$	Direction of $\bar{q}$	Angle of deviation	Relative intensity value	Ratio of the elastic constants determined
Crystal axis coinciding with the vertical axis of the camera	Direction of the Incideam					
[00·1]	Incident beam making 6° with [10·0]	$2.3 \times 10^{-6} \text{cm}^{-1}$	Along the vector corresponding to (40·0) node	48°0'	0.40	$\left. \begin{array}{l} C_{11}/C_{66} \\ = 2.82 \end{array} \right\}$
"	"	$1.1 \times 10^{-6} \text{cm}^{-1}$	Normal to [00·1] and the vector corresponding to (40·0) node	50°15'	4.8	
[11·0]	Incident beam making 25 36' with [00·1]	$0.98 \times 10^6 \text{cm}^{-1}$	Along the vector corresponding to (40·0) node	51°12'	1.9	$\left. \begin{array}{l} C_{11}/C_{44} \\ = 1.54 \end{array} \right\}$
"	"	$0.49 \times 10^6 \text{cm}^{-1}$	Along a line parallel to [00·1] through (40·0) node	50°15'	11.5	

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## RECENT INVESTIGATIONS INTO THE STRUCTURE OF CELLULOSE AND CELLULOSIC FIBRES

By

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In an earlier publication the presence of a new reflection in the X-ray diffraction patterns of pure cellulose fibres (as for example, cotton, ramie etc.) and jute was reported. The claim has since been disputed by some workers and suggestions have been made that the reflection arises from one or other of the following causes: (a) silver or bromine absorption edge; (b) metallic impurity in the target; and (c) white radiation peak. None of the criticisms appears to be valid because—(a) the reflection has not the slightest resemblance with absorption edge that is characterised as is well known, by sharp boundary tailing off at the short wave length side; (b) the intensity along with the spacing of the reflection is different in samples of different origin, as for example, in ramie film, cotton and ramie fibres; (c) the presence of the reflection in the case of jute has been confirmed by Woods in monochromatic photographs as well as by Geiger counter technique; and (d) in one of our recent experiments the reflection appears on photographs taken using radiation monochromatized by lithium fluoride crystal.

Guinier, Legrand and others while using a different experimental technique further confirmed the presence of the new reflection for jute but reported to have failed to record it for pure fibres. From what we have noticed in a photograph privately sent to us by one of the authors (P. Anzenberger) we have reason to believe that their X-ray diagrams are not of suitable intensity. The results rather lend support to our observation that between jute and ramie the new reflection is stronger in the former.

While agreeing with the authors on their remarks about the lack of purity of cellulose in jute we do not think it justifiable to associate the reflection to any impurity other than that takes part in the building up of the lattice. In this connection we would refer to the idea of mixed crystals as well as a previous work in which the presence of the reflection was reported in monochromatic photographs of celluloses extracted from jute. From an extensive series of studies of diffraction patterns, kinetics of rection, swelling, rupture strength and stress relaxation we have been able to bring out some characteristic differences in the structure of pure celluloses as typified by ramie and that of jute but none of the evidence suggests a separate lattice in the latter. For the results discussed hereunder my thanks are due to Banerjee, Ramaswamy and Roy.

### **Causes of Diffuse Scattering in the X-ray Diagrams :**

The X-ray diffraction diagrams show that for ramie the equatorials reflections as also those in the layer lines to a lesser degree are connected by relatively more intense continuous bands of scattered radiation; whereas for jute the scattering is confined mostly to regions outside the direction of selective reflection. Thus both ramie and jute are imperfect crystals. However, the imperfection in ramie seems to arise from a relatively more distorted lattice in which the cells are identical but displaced from their ideal positions. On the other hand, in jute the main cause of imperfection is the mixed crystals on account of which the cells are not identical so far as the structure factor is concerned although the lattice is more regular compared to ramie. To draw an analogy ramie resembles a cold-worked or strain-hardened metal while jute simulates metallic alloys. At this point it may be mentioned that curiously enough the diffuse scattering of cellulose fibres has hitherto been regarded as due to the presence of a separate amorphous phase, the proportion of which has also been estimated by several chemical and physical methods including one by means of analysis of background radiation in the X-ray diagram. Most of the properties of cellulose mainly moisture absorption, swelling and elasticity have since been ascribed to the amorphous phase, the crystalline parts being assumed as perfect and inviolable to moisture, mild chemical treatment and mechanical stress. Even the possibility of mesomorphic state of different orders so clearly indicated in certain long chain liquid compounds has been ignored. Remembering also that a perfect crystal is an ideal state not attainable in practice and the estimates of the crystalline proportion by various methods disagree widely, the two-phase theory does not seem justifiable. The region between crystallites here is expected to be as ill-defined as that between mosaic blocks in a single crystal or individual crystals in polycrystalline metals.

### **Imperfection Density and Surface Structure :**

Cellulose is composed of chain molecules of different lengths and the building unit of the chains is the glucose anhydride residues joined together by 1-4 linkages. From the known values of the energy,  $6 \times 10^{-13}$  ergs and the equilibrium distance, 1.5 Å of the C-O-bond the strength of a cellulose chain liable to rupture at the C-O-C bridge connecting the glucose rings is calculated to be  $2.4 \times 10^{-4}$  dynes. Assuming the arrangement of the chains in the lattice as given by Meyer and Mark, there are  $3 \times 10^{14}$  chains passing through an area of 1 cm<sup>2</sup>. Thus the calculated strength of cellulose is  $7.2 \times 10^{10}$  dynes/cm<sup>2</sup> which is 8-10 times higher than the observed values for the native fibres. Again, the strength as calculated on the assumption of rupture due to breakages of only secondary valence bonds between the chains is too low. The discrepancy between the experimental and theoretical values can be reconciled if it is remembered that the limit of the breaking strength is determined by the imperfections in the crystals. Similarly, calculation of the strength across the 100 plane of rock salt crystal from its potential energy—interatomic distance curves due to de Boer indicates a wide discrepancy between the theoretical and observed values, the figures being  $2.4 \times 10^{10}$  dynes/cm<sup>2</sup> and  $5 \times 10^7$  dynes/cm<sup>2</sup> respectively. This has also been attributed to crystalline imperfections.

Our investigation into the tensile strength shows that both ramie and jute are brittle and therefore snaps before plastic deformation as a result of concentration of stress at some imperfections or defects in the materials. Applying the theory of extreme values and assuming Gaussian distribution of the imperfection it has been

possible to calculate the numerical density and the most probable strength value of the imperfection. Thus

	No./cc	Most probable strength
Ramie	$18.0 \times 10^6$	8.3 gms/den.
Jute	$4.2 \times 10^6$	6.2 gms/den.

The ramie fibre is characterized by the presence of a far greater number of imperfections. If the imperfections are crystalline in origin and assumed to arise from the flow and sticking together of dislocations of opposite signs as required by the theory of plasticity and work hardening of single crystals and polycrystalline metals due to Bragg, Taylor, Read and others, the difference in the numerical concentrations would suggest a greater plastic deformation and hence strain hardening of ramie in the growth process. This view appears to find support from the microscopical observations of the surfaces of cotton, ramie and jute which show transverse bands in the case of the two purer fibres. In view of the close similarity between fibres and metals at least with regard to the mechanical behaviours, as can be safely assumed, it will not be unreasonable to regard the transverse surface markings as identical to the slip bands in crystal and metals due to plastic flow. The qualitative estimate of the imperfection density of cotton, ramie and jute using Wakeham's data for cotton and those from our experiments with ramie and jute indicates that cotton is the most imperfect while jute is the least of the three. These considered along with the electron microscopic observations of the external surfaces of the primary wall of cotton due to Rollins *et al* in which there are innumerable transverse bands not extending to the level of the cellulose fibrils in the underlying layers would lead one to consider whether the idea of the plastic deformation and consequent hardening in the growth process applied in these cases and thereby explained the difference in its magnitude between cotton and ramie. The excellent electron micrographs of the secondary walls of cotton, ramie and sisal due to Muhlethaler should also be referred in this connection. It will be seen from these that ramie has highly organized chain bundles compared with cotton indicating a greater perfection; and sisal is a mutually inter-penetrating lignin-cellulose reinforced structure with minute evenly dispersed pores. A jute fibre may be regarded as somewhat similar to sisal so far as the structure is concerned both being ligno-cellulose materials and the electron micrograph suggests that the fibres have a defect structure with some vacant sites in the lattice. The most probable strength value of jute which is less than that for ramie also leads to similar conclusions.

#### Other Characteristics of Cotton, Ramie and Jute :

Comparing the stress-strain curves of jute, cotton and ramie at a low rate of loading it will be seen that jute is the most inextensible of the three fibres. From the analogy with metals and metallic alloys the inextensible and so hard nature of jute can be explained as due to impurity or impurities in the form of lignin and/or hemicelluloses included in the lattice, consideration being given simultaneously to the steric factor involved in the foreign molecules.

Although microscopic observation of ramie and cotton suggests the effect of strain hardening in the growth process the fibres are softer compared with jute and liable to further deformation when immersed in water. This is clearly seen from a comparative study of the X-ray diagrams of the fibre at ordinary and saturated

humidity which shows that for ramie the intensity of the reflections on the equator and layer lines are reduced with increase in the intensities of the accompanying diffused scattering bands as a result of moisture absorption; with jute no such pronounced effect is noticeable. It appears therefore that the lattice of pure cellulose fibres is easily deformable. In support of this contention we have other evidences which are no less powerful. The results of measurement of longitudinal and transverse swelling of ramie and jute in water after due consideration of the effects of morphological factors show beyond doubt that the secondary wall swells much less in the case of jute. Further, the study of kinetics of acetylation of cotton and jute under various conditions of concentration and temperature of acetylating liquor and initial moisture content of the samples suggests two different mechanisms of penetration of the reacting molecules. According to this the penetrant molecules exchange places with the fibre molecules in cotton while they migrate into the sites ready to receive them in jute. Activation energy of acetylation as calculated is : cotton - 16782 cal/mole and jute - 12816 cal/mole. The difference is certainly due to the energy expended in cotton for pushing apart and accommodation of acetyl groups. For cotton the shapes of the acetyl-time curves are similar to those for concentration dependent and anomalous diffusion the theory of which has been developed by Crank, Hartley and others; while for jute the curves resemble those for zeolitic diffusion as extensively discussed by Barrer and others in connection with their work on minerals.

The relaxation of stress measured by us in different aqueous and non-aqueous media as well as at different temperatures shows clearly that the energy of bonding is greater for jute, the relaxation after a given time being less. The figures for relaxation (i. e. relative decrease of force) per °C rise of temperature are : ramie -  $288 \times 10^{-6}$  and jute -  $48 \times 10^{-6}$  the specimen length of each being 6 cm.

#### Effect of Moisture :

A fibre relaxed to equilibrium at either 75% or 0% relative humidity has been observed to retract when immersed subsequently in dry benzene. This indicates that the solvent molecules combine with and remove the water molecules even when the residual concentration of moisture is very low (e. g. less than 0.5%) as in the fibre conditioned at 0% relative humidity. The results tend to suggest that contrary to the current opinion water and benzene can enter into combination with the cellulose crystals. With a view to obtaining the more direct evidence we have taken X-ray photographs of a sample of ramie fibre at first conditioned at room humidity and again when immersed in benzene. The sharp photograph of the fibre in benzene compared with that at room humidity confirms our original suggestion regarding accessibility of the cellulose lattice to water and benzene molecules.

Now the structure of native cellulose due to Meyer and Mark in which the cellobiose units are mutually hydrogen-bonded in the ab plane, the shortest atomic distance being  $2.5\text{\AA}$  and the nearest atomic distance in the bc plane is  $3.1\text{\AA}$  leaves hardly any room for benzene molecules to take part in the lattice. The water molecules on account of their small size, may however enter into Meyer and Mark cells. Yet it is not easy to explain how they can snap the hydrogen bonds and distort the lattice unless one assumes that the cellulose chains are not hydrogen-bonded in the dry state but irregularly twisted at the lattice points. The ease of removal of water from the lattice as with benzene leads to suggest that the water is combined loosely. As a parallel example we may refer to some of the zeolitic minerals in which water may enter or leave freely with the associated swelling or deswelling of the structure.



In the light of the hitherto accepted interpretation cellulose samples of different origin are regarded as different only in respect of orientation and perhaps crystal size. We have, however, noted that there are more basic differences in the structure as can be seen from the intensity and spacing of the new reflection. Thus, for ramie film, cotton and ramie fibres the following order has been observed :

	<i>Intensity</i>	<i>Spacing</i>
Ramie film :	strong	12·8Å
Cotton fibre :	medium	13·1Å
Ramie fibre :	weak	13·7Å

Considered along with the observation that absorption of moisture increases the spacing (e.g. in cotton from 13·1Å at room humidity to 13·4Å under saturated condition) as well as distorts the lattice resulting in increased diffuse scattering and correspondingly reduced intensity of the reflection, the above can be explained for the moisture absorption and swelling increases in the same order from ramie film to ramie fibre. But it is not clearly understood why the different samples vary with regard to the factors just mentioned. There is however the possibility of mixed crystallization with varying quantity of non-cellulosic substance which is perhaps relatively more hygroscopic, the case being somewhat similar to the solid solution of metals in which there is expansion or contraction of lattice by the presence of alloying impurity. In this regard the ramie film on account of its being prepared by the hydrolytic degradation method is perhaps the purest form. The extreme degree of mixed crystallization is noticed in either native or completely delignified jute having the moisture content, non-cellulosic impurity and generally diffuse scattering at their maximum. As an evidence in support of the assumed hygroscopicity of the impurity we may refer to the work due to Scott on the X-ray study of pure xylan. The unit cell expands on moisture absorption as indicated below :

	a	b	c	$\beta$
Dehydrated xylan :	7·6Å	10·2Å	6·7Å	83°
Xylan at room humidity :	8·0Å	10·2Å	7·0Å	87°

#### Probable Crystal Symmetry :

The lattice parameters at room humidity as previously given (Sen and Roy 1954) are as follows :

	a	b	c	$\beta$
Native ramie :	15·8Å	10·3Å	12·5Å	60°
Merçerized ramie :	16·3Å	10·3Å	9·0Å	64°

The calculated and the observed values of the spacings and their indices as have been given earlier (Sen and Roy 1954) are shown in Table 1 and 2. Consistent with the density of the materials, the number of cellobiose units per cell should be 4.

For the distorted lattice of cellulose it is rather difficult to determine the space group. But the study of the relative intensities of the reflections from native and mercerized ramie (Tables 1 and 2) leads to the following conclusion. The space lattice appears to be primitive as suggested from the presence of reflections corresponding to  $h+l=\text{odd integer}$ ,  $k=0$ .

Table 1.  $hkl$ ,  $d_{\text{cal}}$  and  $d_{\text{obs}}$  Values (Native Ramie)

$hkl$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$
100 (W)	13.68	13.70
001 (VW)	10.82	10.80
200	6.84	7.50
201 (VW)	7.74	
102	5.87	6.01
202 (S)	5.90	
002 (S)	5.41	5.43
303	3.93	3.96
402 (VS)	3.87	
404 (W)	2.79	2.65
606 (W)	1.96	1.96
014 (W)	2.62	2.64
211 (W)	6.19	6.15
221 (M)	4.29	4.31
321	2.95	2.88
023 (W)	2.96	
231 (M)	3.14	3.22
132 (W)	2.69	2.65
331	2.87	2.96
032 (W)	2.90	
142 (W)	2.21	2.18
341	2.31	2.35
042 (VW)	2.33	

VW=very weak, W=weak, M=medium, S=strong, VS=very strong.

Table 2. hkl,  $d_{\text{cal}}$  and  $d_{\text{obs}}$  Values (Mercerised Ramie)

hkl	$d_{\text{cal}}$ (Å)	$d_{\text{obs}}$ (Å)
100 (W)	14.65	14.60
200 (S)	7.33	7.35
102 (VS)	4.39	4.42
202 (VS)	4.46	
002 (VS)	4.04	4.03
003 (VW)	2.70	2.66
404 (M)	2.23	2.21
210 (W)	5.97	6.02
012 (W)	3.77	3.78
412 (VW)	3.41	3.38
212 (VW)	2.90	2.91
312 (W)	2.52	2.57
513 (W)	2.56	
613 (W)	2.35	2.39
021 (S)	4.34	4.35
221 (M)	3.40	3.41
321 (W)	2.92	2.98
223 (W)	2.59	2.58
023 (VW)	2.39	2.38
031 (M)	3.16	3.14
132 (W)	2.71	2.62
431 (W)	2.62	

VW=very weak, W=weak, M=medium, S=strong, VS=very strong

It appears that the cause of the weak intensity of the new reflection lies in the symmetry of the crystal and also the dissipation of energy in the diffuse scattering associated with the distortion of the lattice. The jute lattice is rather rigid and so gives a relatively stronger reflection. To account for the rigid lattice of jute it should be considered whether in this case there is sufficient crystalline inclusion apart from xylan and consisting of molecules of bigger size as a result of which the nearest atomic distance in ab and/or ac plane is shorter and therefore primary valence type bonding is present.

#### Partially Acetylated Fibres :

Further evidence for the presence of the new reflection is provided by the X-ray diagrams of partially acetylated (less than 20% acetyl) cotton, ramie and jute. It

will be seen that there is a diffuse band in the region corresponding to the sharp reflection in the native cotton and ramie; in jute the reflection becomes sharper as a result of such treatment. The reason is obvious when the effect is considered from the previously discussed characteristic response of the two types of fibres. The swelling treatment involved in the acetylation disturbs and distorts the lattice planes of the pure cellulose specimens; whereas jute being rather rigid does not show such distortion and disturbance but indicates the general increase in the intensity of the reflection the cause of which perhaps lies in the increased structure factor as a result of acetylation. In this connection we might add that the mild acetylation treatment as used cannot be assumed even for the sake of argument to regenerate a cellulose of altogether different structure.

### CONCLUSION

We thus find that the experimental evidences in support of the new structure as proposed earlier are quite strong. The theoretical justification for it also appears to be sound. The proposed structure not only explains the new facts regarding intensity and spacing changes in the X-ray diagrams hitherto unobserved but opens the field for further work in explaining the effect of moisture absorption, non-cellulosic inclusion and mechanical stress. The possibility of connection between the molecular structure and surface property is tentatively suggested, which is more or less an established fact in the case of metals and some inorganic crystals. It is expected that future work using recent techniques of X-ray, electron microscopy and infra-red absorption would unfold many of the yet unresolved details of the structure of cellulose and cellulosic fibres.

# ON THE THERMOLUMINESCENCE AND TRAPPING MECHANISMS OF ALKALIHALDES

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## ABSTRACT

Thermoluminescence of sodium chloride (Harshaw) excited by 5-10 KV cathode rays at liquid nitrogen temperature has been measured with different rates of heating. The experimental procedure is similar to that developed by Bose & Sharma (1950, 1953, 1955). The determination of 'S' and 'E' separately from the shape of the thermoluminescence curves with different rates of heating has been attempted by extending the method originally due to Randall and Wilkins (1945). On analysing the experimental results, it has been found that the value of 'S', (in the way it has been introduced in the theory of phosphorescence and thermoluminescence) appears to be rather strongly dependent on temperature and rate of heating. This implies that the existing methods of determining trap depths may not be applicable in all cases, though in particular types of phosphors the methods are expected to yield correct results. It has been suggested that the explanation for such difference in behaviour should be found in the characteristics of the corresponding trapping mechanisms. The low temperature glow peak of sodium-chloride which forms the subject of investigation in the present paper, is due to a  $V_1$ -centre i. e. a 'hole' trapped in a positive ion vacancy; the behaviour of such a trapping mechanism, where trap depth itself is likely to be dependent on temperature and environment, is expected to be different. The effect of particle size and the thickness of the sample has also been discussed in relation to the rate of heating.

## INTRODUCTION

Thermal and optical stimulation of a phosphor which has been previously excited by ultraviolet radiations, X-rays or any high energy particles, offers a straight forward method of studying the behaviour and characteristics of trapping mechanisms of the various types of phosphors under different conditions. The corresponding trap depths responsible for energy storage in phosphors on excitation and subsequent release of energy with or without stimulation, can also be estimated in many simple cases. The decay of long period phosphorescence intensity is supposed to be due mainly to the mean time spent by the captured electrons in the trapping states inside the crystal. Assuming that the probability of escape from a trap of depth 'E' at a temperature 'T' be given by,  $Se^{-E/KT}$ , the decay law for phosphors in which the probability of retrapping is negligible, should be given by

$$I_t = I_0 \exp [-Ste^{-E/KT}]. \quad (1)$$

For substances in which the probability of retrapping before reaching an emitting centre is considerable, the decay law (Garlick 1947) becomes,

$$I_t = \frac{n_0^2 S e^{-E/KT}}{N \left( 1 + \frac{n_0}{n} S e^{-E/KT} \right)^2} \quad (2)$$

where,  $N$  = number of traps in the phosphors,  $n_0$  = numbers of electrons initially trapped.

The variation from the exponential and bimolecular decay laws as is actually observed in many cases, is generally explained as due to non-saturation effects and presence of trapping states of different depths.

Various authors (Randall & Wilkins, 1945; Garlick, Gibson, 1948; Urbach, F, 1930; Bose [unpublished work]), have tried to estimate the trap depths of phosphors by different methods which are essentially based on the same principle. If the sample is steadily heated during phosphorescence the after glow intensity at any temperature is given by

$$I = n_0 C \exp \left[ - \int \frac{S}{\beta} e^{-E/KT} dT \right] S e^{-E/KT} \quad \dots \dots \dots (3)$$

for a single trap depth 'E' in the absence of retrapping,  $\beta$  being the rate of heating.

When the effect of retrapping, is not negligible, the expression becomes (Garlick, 1948)

$$I = \frac{N S e^{-E/KT}}{\left( \frac{N}{n_0} + \int \frac{S}{\beta} e^{-E/KT} dT \right)^2} \quad \dots \dots \dots (4)$$

According to Randall & Wilkins, (1945), the equation (3) can be reduced approximately to the form

$$E = K T_G \text{ Log } S. [1 + f(S, \beta)] \quad \dots (5)$$

where  $T_G$  is the temperature corresponding to maximum emission. 'log S' and  $f(S, \beta)$  can be approximately estimated by performing the experiment under different conditions.

The method followed by Garlick is to draw a set of theoretical curves for (3) and (4) for different values of 'S' and 'E' for a particular rate of heating so that the values of 'E' and 'S' could be estimated by comparison with the experimental thermoluminescence curve. The other alternative method followed by many authors is to plot  $\log I$  'vs'  $\frac{T}{T}$  for the early part of the thermoluminescence curve and

determine the 'E' from the corresponding slope of the plotted curve. Hill and Schwed, (1955), utilised this method in studying different parts of the thermoluminescence curve by alternate heating and cooling. The different methods in practice have been ably summarised by Curie & Curie (1955) and they have also developed a method of determining 'E' by varying the rate of heating. One of the present authors (Bose unpublished work) has also developed a number of methods for determining 'S' and 'E' separately from thermoluminescence and decay experiments. The following expressions can be deduced from (1) and (3) or (4), assuming that 'S' varies rather slowly in the temperature as has been found by Randall and Wilkins (1945) for ZnS,

$$\frac{E}{KT^2} = P + \frac{\alpha(T)}{\beta} \quad (6)$$

$$\text{Exp} \left[ \frac{E}{K} \left( \frac{1}{T_G} - \frac{1}{T'_G} \right) \right] = \frac{\beta}{\beta'} \cdot \frac{I_G^2}{I'^2_G} \quad (7)$$

$$E/KT^2 = \frac{\beta P - \beta' P'}{\beta - \beta'} \quad (8)$$

$$E/KT^2 = \frac{\beta P I'^{\frac{1}{2}} - \beta' P' I^{\frac{1}{2}}}{\beta I'^{\frac{1}{2}} - \beta' I^{\frac{1}{2}}} \quad (9)$$

$\alpha(T)$  = after glow decay constant  $S e^{-E/KT}$  at temperature 'T' where

$$P = \frac{1}{I} \cdot \frac{dI}{dT}$$

$\beta$  and  $\beta'$  are the rates of heating while  $I$  and  $I'$  are the corresponding thermoluminescence intensity, and the eq. (9) is applicable for retrapping only.

The present authors have been engaged in determining the values of 'E' and 'S' from thermoluminescence and phosphorescence of alkali halides under cathode rays with the help of the expressions (6), (7), and (8); as the effect of retrapping has been found to be negligible in such phosphors the equation (9) was not necessary. It has been found that the values obtained from different parts of the same glow peak varies within wide limits beyond the range of experimental error. There is remarkable disagreement between the values of E or S determined by various authors. According to Hill and Schwed the value of 'S' varies between  $10^{10}$  to  $10^{17}$  in the case of sodium chloride. It is doubtful whether such wide variations can always be attributed to the past history of the sample which being different in each case may, in an unknown way, be responsible for such effects. It therefore seemed necessary to examine the validity of extending the methods to the case of these phosphors.

As there is sufficient experimental evidence that the effect of retrapping is negligible in these phosphors, the equation (3) has been used for this purpose and this can be written in the form

$$\left. \begin{aligned} E/KT^2 - \frac{1}{I} \cdot \frac{dI}{dT} &= \frac{S}{\beta} e^{-E/KT} - \frac{1}{S'} \cdot \frac{dS}{dT} \\ \frac{\beta E}{KT^2} - \frac{1}{I} \cdot \frac{dI}{dt} &= S e^{-E/KT} - \frac{1}{S'} \cdot \frac{dS}{dt} \end{aligned} \right\} \dots \dots \dots (10)$$

If 'S' be independent of, or a slow function of temperature and range of temperature involved in the measurement small, the contribution due to the changes in  $\frac{1}{S} \frac{dS}{dt}$  can be neglected so that

$$\left( \frac{\beta E}{KT^2} - \frac{1}{T} \frac{dI}{dt} \right) e^{E/KT} = S. \quad \dots\dots\dots(11)$$

In the present work thermoluminescence of sodium chloride excited by cathode rays at liquid nitrogen temperatures has been studied for different rates of heating with a view to study the consistency of the relations, (10) and (11).

#### EXPERIMENTAL METHOD

The demountable cathode ray tube with double walled tubular sample holder of silver as used by Bose (1953), Bose & Sharma (1950) has been used in this investigation. The sample was taken in the form of a thin layer of the powdered specimen rubbed on the sample holder; thus better uniformity of temperature at comparatively higher rates of heating could be attained (Bose, 1950). Sodium chloride used in this experiment was obtained from Harshaw chemical in the form of single crystals. The specimen was excited by low energy cathode rays (5 kv) at liquid nitrogen temperature; the thermoluminescence intensity and the temperature of the phosphor was recorded simultaneously on a photographic paper mounted on a rotating drum; the photomultiplier tubes 1P 21, 931A etc. with the usual standard type of electronic circuits were used for this purpose and the details of the experimental procedure were similar to that described by Bose (1950).

#### RESULTS AND DISCUSSIONS

The thermoluminescence of sodium chloride excited by cathode rays at a liquid nitrogen temperature show three glow peaks with temperatures for maximum glow at  $164^\circ K \pm 1^\circ K$ ,  $245^\circ K \pm 2^\circ K$  and  $600^\circ K$  (nearly). The glow peaks are all separated from each other (Bose 1955) and the third peak is generally too poor to be recorded for sample excited at liquid nitrogen temperature; the glow peak at the lowest temperature ( $164^\circ K$ ) is much more pronounced than the other. The measurements have been carried out on this prominent peak only and were confined to temperatures between  $148^\circ K$  to  $187^\circ K$  (nearly the half width of the glow peak). Thus the effect of the other glow peaks can be assumed to be negligible. The traces of the typical records of the relevant portion of the thermoluminescence curves for different rates of heating are shown in Figs. 1—4. The measurements for different temperature and various rates of heating are given in Table I. In the last column of Table I are given the values of the expression,

$$\left( \frac{\beta E}{KT^2} - \frac{1}{T} \frac{dI}{dt} \right) \exp [E/KT], \text{ (say, } ye^{E/KT} \text{ )};$$

'E' in this expression has been taken to be equal to  $21.KT_z$  which is an approximate formula for  $S \approx 10^9 \text{ sec}^{-1}$  (Leverenz 1950). The error involved in the value of 'E' so determined would be rather small and the corresponding changes in the value of 'y' are not sufficient to account for the differences observed in the value of y for the same curve at various temperature and for different rates of heating at the same temperature. The values of 'y' for different temperatures have been plotted against temperature on a logarithmic scale and the nature of the graphs so obtained for different rates of heating is shown in fig. 5. It may be easily seen that there is a regular change in the value of 'y' within the same curve as well as for different rates of heating at the same temperature. These preliminary results seem to indicate that 'S' is rather strongly dependent on temperature as well as rate of heating.



Thus the results seem to confirm the suspicion that the present methods of determining the trap depths of phosphors, based primarily on the fact that the rate of release of electrons is proportional to  $\text{Se}^{E/KT}$  may not be suitable in all cases.

The possible explanation for such a behaviour in the sodium chloride may be found in the mechanism responsible for this glow peak. There is experimental evidence to believe that this glow peak in sodium chloride is due to  $V_1$ -centres i.e. positive holes trapped at positive ion vacancies caused by excitation. On thermal stimulation the positive hole is released from the trap and is free to wander through the lattice until it reaches a position where recombination occurs producing emission. The stability of such trapping centres is strongly dependent on the temperature and environment which implies that the trap depth 'E' is determined by the temperature and possibly to a certain extent by the concentration also. Further the value of 'S' for a trapped hole may also be different from that for a trapped electron. Further the continuous variation in the temperature of the phosphor inherent in the method makes it difficult for the sample to attain equilibrium or uniform temperature throughout its entire volume at any stage; the effect will depend on the thickness of the layer and particle size of the phosphor. The reasons for the dependence of 'S' on the rate of heating may thus be understood.

The situation will however be different in cases of those trapping states which are similar to the forbidden or metastable optical states; long period phosphorescence of organic phosphors and activated phosphors having localised impurity levels may be due to such traps. In these cases the trap depths are comparatively sharp and practically independent of temperature. The present methods of determining trap depths from thermoluminescence data are expected to be quite suitable in such cases. Further investigations are in progress to examine the various aspects of the problem.

TABLE I

*Data corresponding to Fig I.*

$\beta$  = rate of heating =  $1.47^\circ\text{C}/\text{sec}$ .

$T_{\text{max}}$  = Peak temp =  $165^\circ\text{K}$

$E = 21KT_{\text{max}} = 0.4785 \times 10^{-12}$  ergs.

T°K	$\frac{1}{I} \frac{dI}{dt}$ $\text{sec}^{-1}$	$\frac{E}{KT^2} \beta$ $\text{sec}^{-1}$	$\gamma$ $\text{sec}^{-1}$
149.6°k	0.1972	0.2216	0.0244
154	0.1766	0.2148	0.0382
156.4	0.1617	0.2083	0.0466
160.0	0.1029	0.1990	0.0961
162.4	0.0342	0.1920	0.1578
165.0	0	0.1871	0.1871
168.4	-0.05145	0.1797	0.23115
172.0	-0.0818	0.1722	0.2540
174.3	-0.1078	0.1677	0.2755
177.0	-0.1258	0.1626	0.2884
180	-0.1457	0.1572	0.3029

TABLE II

*Data corresponding to Fig. 2.* $\beta$ =rate of heating=2.62°C/sec. $T_{\max}=163.2^{\circ}\text{K}.$  $E=0.4728 \times 10^{-12}$  ergs.

$T^{\circ}\text{K}$	$\frac{1}{I} \frac{dI}{dt}$	$\frac{E}{KT^2} \beta$	$y$
149.8	0.3234	0.3996	0.0762
153.9	0.2830	0.03785	0.0955
156.4	0.1887	0.3667	0.1780
157.9	0.1415	0.3613	0.2198
160.1	0.0671	0.3503	0.2832
163.2	0	0.3376	0.3376
165.2	-0.0452	0.3286	0.3738
167.9	-0.0959	0.3182	0.4142
173.7	-0.1258	0.2973	0.4231
184	-0.2096	0.2650	0.4746
187.7	-0.2902	0.2546	0.5448

TABLE III

*Data corresponding to Fig. 3.* $\beta$ =rate of heating=3.6°C/sec. $T_{\max}=165.2^{\circ}\text{K}$  $E=0.479 \times 10^{-12}$  ergs.

$T^{\circ}\text{K}$	$\frac{1}{I} \frac{dI}{dt}$ sec <sup>-1</sup>	$\frac{E}{KT^2} \beta$ sec <sup>-1</sup>	$y$ sec <sup>-1</sup>
149.7	0.4541	0.5573	1.032
154.2	0.3620	0.5254	0.1634
159.2	0.1925	0.4926	0.3001
165.2	0	0.4500	0.4500
177.8	-0.1063	0.3957	0.5012
184.1	-0.2065	0.3685	0.5750
190.0	-0.4062	0.3458	0.7520

TABLE IV

*Data corresponding to Fig. 4.*

$$\beta = 5.13^\circ\text{C/sec.}$$

$$T_{\text{max}} = 164^\circ\text{K.}$$

$$E = 0.4755 \times 10^{-12} \text{ ergs.}$$

$T^\circ\text{K}$	$\frac{1}{I} \frac{dI}{dt}$ sec <sup>-1</sup>	$\frac{E}{K'T^2}\beta$ sec <sup>-1</sup>	$\gamma$ sec <sup>-1</sup>
149.6	0.5899	0.7879	0.1980
153.2	0.5022	0.7572	0.2490
159.2	0.1753	0.6955	0.5202
164.0	0	0.6130	0.6130
171.8	-0.0266	0.5974	0.6240
175.0	-0.1622	0.5758	0.7380
178.2	-0.2460	0.5550	0.8010
181.1	-0.2926	0.5374	0.8300

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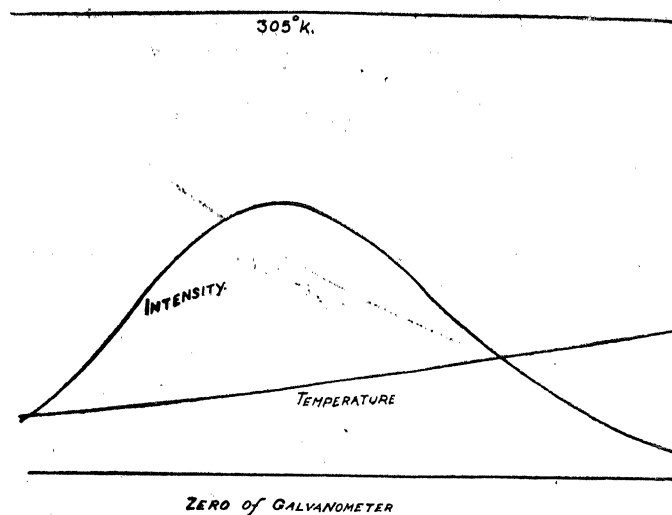


Fig. 1.  
Thermoluminescence Curve  
of NaCl (Harshaw)  
Excited at 86°K  
rate of heating = 1.47°

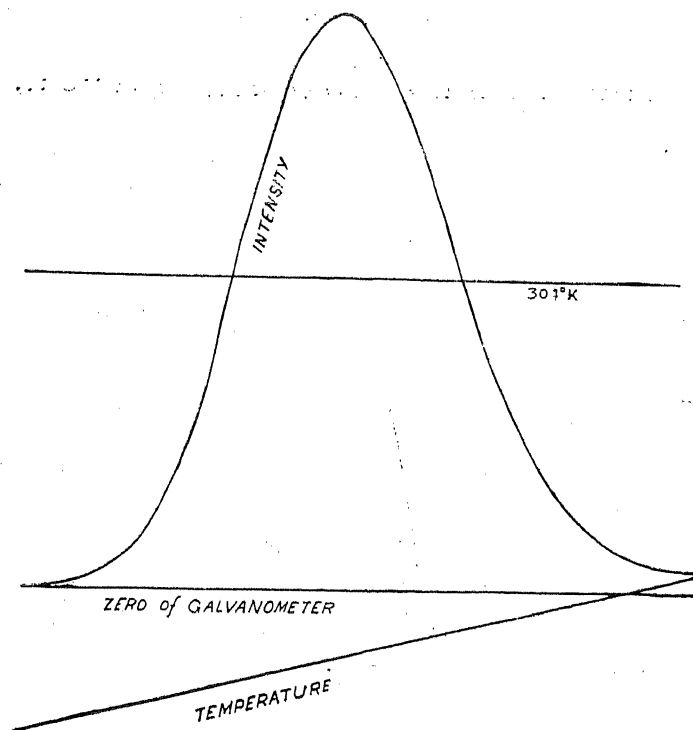


Fig. 2.  
Thermoluminescence Curve of NaCl for  $\beta = 2.62^\circ \text{C/Sec.}$

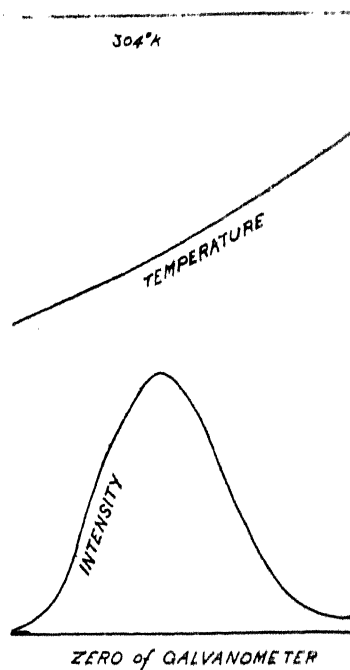


Fig 3.  
Thermoluminescence Curve of NaCl for  $\beta=3.6^{\circ}\text{C/Sec.}$

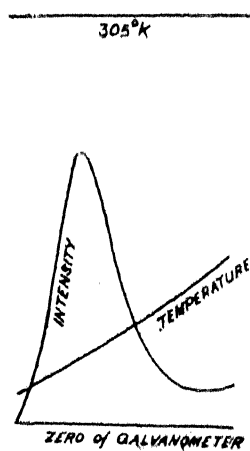


Fig 4.  
Thermoluminescence of NaCl for  $\beta=5.13^{\circ}\text{C/Sec.}$

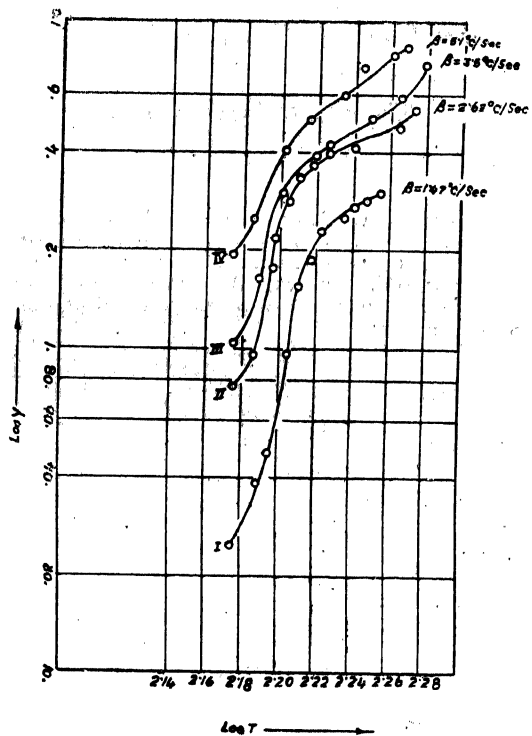


Fig 5

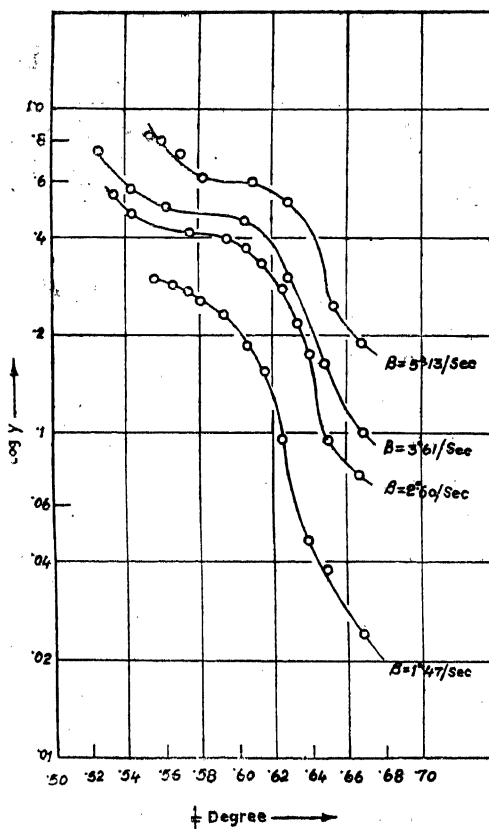


Fig. 6

# LATTICE DISORDERS IN KAOLINITE

By

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(Communicated by Prof. K. Banerjee)

•Read at the Silver Jubilee Session on 27th December 1955 at the University of Lucknow.

## SUMMARY

Microphotometric records of X-ray diffraction photographs of Kaolinite have been critically examined. By eliminating the broadenings due to geometrical factors as well as to particle size effects from the experimental curves, the intensity distributions due to lattice defects only have been studied. It has been observed that a disordered lattice is coexistent with the ordered one. The disordered lattice is found to consist of a stacking of (001) planes having random orientation. Occasional shifts by  $1/3$  'b' in the 'b' direction have also been observed.

## INTRODUCTION

Crystals having layer type lattice are prone to develop structural defects. The intraplanar binding is generally strong whereas the interplanar binding is, as a rule, weak. Consequently, there is every likelihood of one layer being either displaced, rotated or shifted with respect to a consecutive layer. In fact such defects have been detected in many layer type lattices e.g. of graphite, hexagonal cobalt, montmorillonite etc.

Kaolinite has been found by Gruner (1932) and Brindley and Robinson (1946) to be composed of stackings of 'Kaolin' layers proposed by Pauling (1930). The 'Kaolin' layer consists of a hexagonal network of Si-O tetrahedron with a superposed layer of Al-O,OH octahedra sharing the oxygen atoms at the apices of the tetrahedron. It is natural to expect mistakes in the stacking of these layers and such mistakes have actually been observed in associated minerals like fireclay and metahalloysite. It has been our aim in this paper to investigate whether such defects occur in the layer lattice of 'Kaolinite'.

It is well known that the broadness of a line in a powder diffraction diagram of a polycrystalline substance is due to three factors viz., (1) Geometrical broadening due to finite slit width, sample size, divergence of the beam etc. (2) Particle size broadening due to smallness of crystallite size and (3) Defect broadening due to extension in the reciprocal lattice space around reciprocal lattice points caused by mistakes in periodicity. In this investigation we have determined the broadening due to lattice defects by eliminating from the observed line broadening those due to the other two causes.

## II. EXPERIMENTAL

### 1. Characteristics of the powder pattern.

Several samples of Kaolinite from Singbhum, India were examined by the X-ray powder diffraction method. Some of the samples were mixed up for the purpose of calibration with powdered Aluminium in the mass ratio of Kaolinite: Aluminium as 4:1. For the purpose of taking diffraction diagrams filtered copper

as well as Molybdenum rays were used. The camera radius was approximately 5 cms.

The distribution of intensity in the powder patterns was determined with the help of a Kipp and Zone recording microphotometer. Some of the lines however were re-examined with the help of a Hilger non-recording microphotometer.

The lines in the diffraction pattern were indexed on the basis of the unit cell proposed by Brindley and Robinson (1946). The microphotometric curves for the different planes (Fig. 1) show that from the point of the line profile the reflections can be divided into three categories

(1) *The basal reflection.*—The line profiles are slightly asymmetrical and the reflections occupy a wide scattering domain in the reciprocal space.

(2) *Reflections having  $l=0$ .*—The intensity distribution curves rise rather steeply, from the low angle side and tail off in the large angle side. The (130), (200), (060) and (300) reflections are rather sharp whereas the (110), (240) and (310) reflections are comparatively broad.

(3) *Other reflections.*—The line profiles of remaining reflections are dissimilar in nature. The (133), (134) and (033) reflections are more or less symmetrical and comparatively sharp. Other reflections are asymmetrical and broad.

## 2. Correction for Geometrical broadening.

Geometrical broadening was accounted for by taking X-ray diffraction photograph of powdered quartz in the same camera and under identical conditions of radius of sample cylinder, slit width of the collimator etc. Due to the excessive hardness of quartz, the particle size remained rather big. Thus there could be no possible size broadening of the diffraction lines. Moreover since the quartz sample was specially selected for its perfection in crystal structure, there could not be any defect broadening. Thus, the broadening of the lines in the diffraction pattern was entirely due to geometrical reasons. The geometrical broadening at various angles was determined microphotometrically from the diffraction pattern and plotted against the angles.

## 3. Correction for particle size broadening.

(a) *The determination of particle size*—The apparent particle size  $\epsilon$  was determined from the well known Scherrer formula  $\epsilon = \frac{\lambda}{\beta \cos \theta}$  where  $\lambda$  is the wave length used,  $\beta$  the half intensity width of the reflection and  $\theta$  the Bragg angle. From  $\epsilon$ , the real particle dimension  $p$  was determined with the help of an equation developed by Stokes and Wilson (1942) according to which

$$\epsilon = \frac{\sqrt{(h^2 + k^2 + l^2)} (6h^3 - 2hk + kl - 2lh)}{6h^3} p$$

( $hkl$ ) being the indices of the reflection. The indices are in the order  $h \geq k \geq l$ . The physical meaning of  $p$  is that it signifies the linear extension of the crystallite in the ( $hkl$ ) direction.

(b) *Line profile for particle size extension.*—The line profile of an ( $hkl$ ) reflection

$$[111]$$



by a crystalite of particle dimension  $p$  has been deduced by Wilson (1949), according to whom:

$$I(s) = \frac{p^4 (h^2 + k^2 + l^2)^{\frac{3}{2}}}{2 U h} \left[ \frac{1}{\psi^2} \left\{ \frac{h+k+l}{h} - \frac{(h-k)(h-l)}{h^2} \cos 2\psi \right\} - \frac{1}{\psi^3} \frac{hk - 2kl + lh}{h^2} \sin 2\psi - \frac{3}{2\psi^4} \frac{kl}{h^2} (1 - \cos 2\psi) \right]$$

where  $\psi = (\pi p s \sqrt{h^2 + k^2 + l^2})/h$

$U$  is the volume of the unit cell and  $I(s)$  the intensity at a point in the scattering domain at a distance  $S$  from the reciprocal lattice point corresponding to  $(hkl)$ .

The line profile for reflection from  $(110)$  plane of Kaolinite after corrections for geometrical and particle size broadenings are shown in Fig. 2.

### III. DISCUSSION

**1. The Basal Reflection**—The particle size corresponding to  $(001)$ ,  $(002)$  and  $(004)$  reflections have been determined to be 28 A.U., 36 A.U. and 105 A.U. respectively i.e. 4, 5 and 15 layers thick. Whereas the particle size determined from the  $(001)$  and  $(002)$  reflections are not very different, the particle size determined from  $(004)$  reflection is 3 to 4 times bigger. However the particle size determined from the  $(004)$  reflection seems to be more plausible because if the particle were only 3 to 4 layer thick, the 'd' values of the  $(001)$  and  $(002)$  reflections would become larger than usual due to Lennard Jones shift. In the present case  $d_{001} = 7.02$  A.U. and  $d_{002} = 3.53$  A.U. a little less than the usual values of 7.15 A.U. and 3.57 A.U. respectively. So the particle size cannot be as small as determined from the line breadth of  $(001)$  and  $(002)$  reflections. To test this point further microphotographs of several diffraction photographs were examined but the results came to be the same.

**2. Characteristics of non-basal reflections**—In both  $(hko)$  and  $(hkl)$  types of reflections, it is observed that the planes having 'k' as an integral multiple of 3 are rather sharp and symmetrical. This effect is much more pronounced in the case of  $(hko)$  type of reflections. It is further observed that in the case of  $(hko)$  reflections the slope of the microphotometer curve is comparatively steep on the low angle side whereas the curve tails off on the larger angle side. The latter points to the probability of there being a disordered phase coexistent with the normal phase. The disordered phase has random orientation of planes perpendicular to the C-axis. The whole phase can not be completely disordered because, in that case,  $(hkl)$  planes would have been non-existent and the microphotometric curves would rise much more sharply on the low angle side and their tailing off in the large angle side would be much more pronounced.

Regarding the first point namely that only reflections with 'k' a multiple of 3 are sharp and regular, the conclusion that there has been a shift of the planes in the 'b' direction by an amount of  $\frac{1}{3}b$  becomes irresistible. Such displacement will not affect reflections with 'k' an integral multiple of 3 because the atoms by this operation are placed at points capable of making coherent scatterings with respect to similarly situated atoms. In short, such displacement will place atoms in regular lattice points of the unit cell in case of reflections having  $k=3n$ ,  $n=0, 1, 2, 3, \dots$  etc. and the intensity distribution will be symmetrical. In the case of  $k \neq 3n$ ,  $n=0, 1, 2, 3, \dots$  etc., the atoms will not be placed in regular lattice points and incoherent scattering from successive planes will occur, resulting in an asymmetry

in the intensity distribution curve. Such displacements have also been observed by Nakahira (1952) in Montmorillonites. The particle size of the disordered phase has been assumed to be the same as that of the ordered phase. In several cases, the reflections examined, overlapped with other (hkl) reflections. In such cases, the contribution only of the required reflection has been calculated accepting the particle size to be the same for all the overlapping reflections.

#### IV. CONCLUSIONS

The experimental results seem to point to the mutual coexistence between a disordered and an ordered phase in 'kaolinite'. Whereas the ordered phase has been assumed to have the crystal structure due to Brindley and Robinson (1946), the disordered phase has been found to consist of (001) planes being stacked together with regular interplaner distances but randomly oriented with respect to each other. Moreover there seems to be a shift of planes in the 'b' direction by an amount  $\frac{1}{3}b$ .

#### V. ACKNOWLEDGEMENTS

We have great pleasure in recording our grateful thanks to Prof. K. Banerji for encouragement and helpful discussions and to Prof. H. N. Bose for his kind interest in the work.

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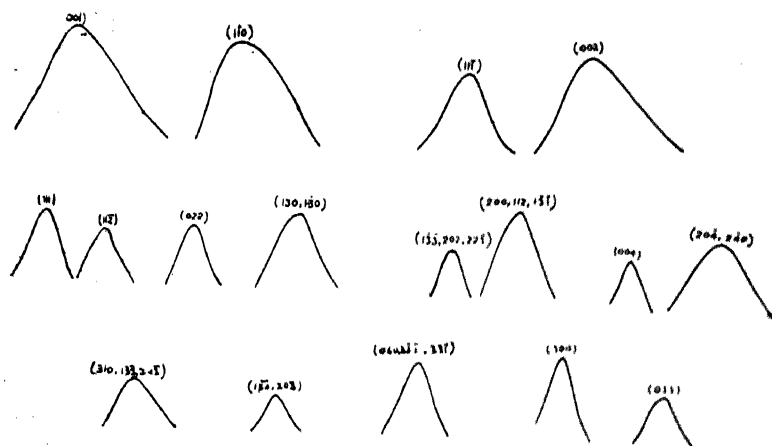


Fig 1.  
Experimental Line Profiles of Several Reflections of Kaolinite.

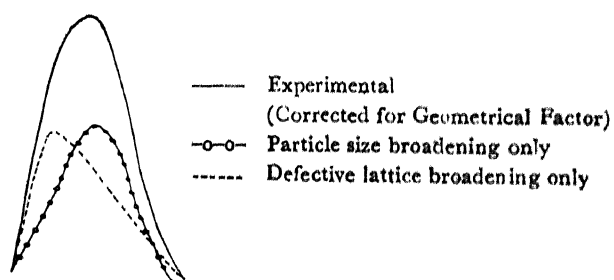


Fig 2.  
Defect Lattice Line Profile of (110) Plane of Kaolinite.

# SPACE GROUP OF O-PHTHALIC ANHYDRIDE

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The crystal structure of O-Phthalic Anhydride,  $C_8H_4(CO)_2O$ , by X-ray diffraction studies has not yet been worked out fully, although morphological and optical data are available, by which it has been shown to belong to the orthorhombic system. Williams, Van Meter & McCrone (1952) found out the axial parameters of the crystal to be  $a=7.90\text{\AA}$ ,  $b=14.16\text{\AA}$  and  $c=5.94\text{\AA}$  by making use of the powder diffraction method. These values were modified by Pandey (1954) by a careful determination from the single crystal rotation photographs about the three crystallographic axes, his values being  $a=7.86\text{\AA}$ ,  $b=14.18\text{\AA}$  and  $c=5.904\text{\AA}$ . From the regularities in the absences of the spots in the normal-beam Weissenberg photographs about the three axes and the Equi-inclination photographs about the  $[001]$  axis, he deduced the space group of O-Phthalic Anhydride to be either  $C_{2v}^0 - P_{na}$  or  $D_{2h}^{16} - P_{nma}$ . As only the latter of these two possesses a centre of symmetry, it was thought worthwhile to perform the statistical tests of Wilson (1949), and Howells, Phillips and Rogers (1950) to test whether the crystal possesses a centre of symmetry or not, and remove the ambiguity in the space group. In the present investigation a critical examination of the intensity distribution in the reflections in the above mentioned Weissenberg photographs was undertaken and the space group of o-Phthalic Anhydride deduced.

## STATISTICAL TESTS OF WILSON AND ROGERS

The relative integrated intensities of the spots in the normal beam Weissenberg photograph about the  $[010]$  axis were eye estimated with the aid of a standard stepped wedge using Cu K-radiation. The intensities with the corresponding structure factors were divided into groups of different  $\sin \theta$  ranges and the Wilson's Ratios, given by  $\rho = (\langle |F|^2 \rangle / \langle I \rangle)$ , for the respective groups obtained. The values of Rogers'  $(z)\%$  were also computed for different planes in each of these groups and the values of  $N(z)\%$  obtained.

## RESULTS

The values of the Wilson's Ratio for the (hol) projection was found to be 0.761, which is in quite a good agreement with the theoretical value of  $\frac{\pi}{4} = 0.785$  for the non-centrosymmetric case.

A plot of Rogers'  $N(z)\%$  against  $(z)\%$ , gives a fairly close fit with the theoretical curve for the non-centrosymmetric case. In fig (1), has been presented the mean curve for (hol) projection.

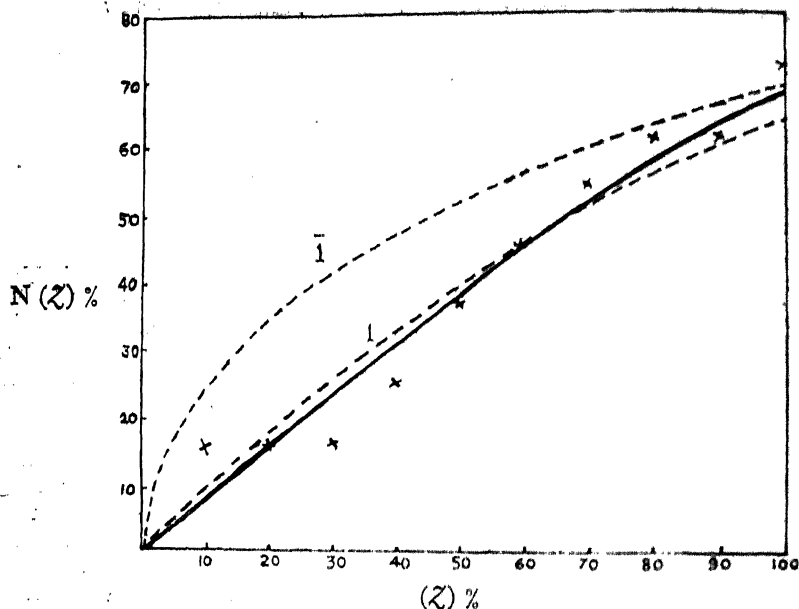


Fig. (1) :  $N(Z) \%$  Values for the (hol) Projection of *O*-Phthalic Anhydride.

The theoretical curves for the centrosymmetric and non-centrosymmetric case are drawn in discontinuous lines.

Thus the space group of *O*-Phthalic Anhydride is shown to  $C_{2v}^9 - P_{na}$ , the non-centrosymmetric of the two.

These tests were also performed for the (hko) projection and the presence of a centric distribution in this projection was confirmed, as it should have been.

Further work on the structure of *O*-Phthalic Anhydride is in progress using Mo-radiation as the number of possible planes in the (hol) projection is fairly low for this crystal for Cu-radiation.

The author is grateful to Prof. K. Banerjee, D.Sc., F.N.I., who suggested this problem, for his guidance throughout the work. Thanks are also due to Shri B. V. R. Murty and Shri S. C. Chakravarty for their interest in the work, and to the Government of India, Ministry of Education for financial assistance.

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